

FREYDLIN, A.Ya., kandidat tekhnicheskikh nauk.

Technological productivity of stamping automobile bodies. Avt.1  
trakt.prom. no.4:34-39 Ap '57. (MLRA 10:5)

1.Gor'kovskiy avtozavod imeni Molotova.  
(Automobiles--Bodies)  
(Sheet-metal work)

FREYDLIN, Abram Yakovlevich, kand.tekhn.nauk; SVERDLOV, M.I., kand.  
tekhn.nauk, red.; KUBNEVA, M.M., tekhn.red.

[Gold forging techniques; stenographic record of a report]  
Tekhnika kholodnoi shtampovki. Stenogramma doklada. Lenin-  
grad, Leningr.dom nauchno-tekhn.propagandy, 1958. 47 p.  
(MIRA 12:9)

(Metals--Cold working)

(Sheet-metal work)

KISELEV, I.I.; BORISOV, N.I.; YASINOVSKIY, B.S., inzh.; SANNIKOV, Yu.K., inzh.; SOKOLOV, V.A., inzh.; LEVCHENKO, L.D., inzh.; NALOYEV, G.A., inzh.; CHICHAKOV, K.K., inzh.; BARYKIN, V.I., inzh.; FREYDLIN, A.Ya., inzh. GULYAYEV, A.I., inzh.; STIGNEYEV, Ya.F., inzh.; SHAGANOVA, K.N., inzh.; KHELIMSKIY, I.Ye., inzh.; AVROV, A.N., inzh.; DEMIDOVA, M.I., inzh.; NIKIFOROVA, Ye.D., inzh.; KLIBANOVA, F.I., inzh.; CHIVEUNOV, K.I., inzh.; STOROZHKO, I.G., inzh.; NOVAKOVSKIY, Ye.Ye., inzh.; GOYKHTUL', A.O., inzh.; TARASOV, A.M., inzh.; SHISHKO, A.P., inzh.; UVAROV, P.T., ekonomist; DRAGUNOV, M.V., ekonomist; KARANDASHOV, A.A., ekonomist; KONKIN, M.V., ekonomist; GOREV, M.S., ekonomist. Primarni uchastnye: LAPIN, T.I.; RAMENSKIY, Yu.A.; KADINSKIY, B.A.; SOKOLOV, S.D.; STOROZHKO, I.G.; POMINYKH, A.I.. POLYAKOVA, N., red.; SMIRNOV, G., tekhn.red.

[Organization and improvement of production; practices of the Gorkiy Automobile Plant] Organizatsiia i sovershenstvovanie proizvodstva; opyt Gor'kovskogo avtozavoda. Moskva, Gos. izd-vo polit. lit-ry, 1958. 332 p. (MIRA 12:2)

1. Direktor Gor'kovskogo avtomobil'nogo zavoda (for Kiselev).
2. Glavnyy inzhener Gor'kovskogo avtomobil'nogo zavoda (for Borisov).
3. Gor'kovskiy avtomobil'nyy zavod (for all except Kiselev, Borisov, Polyakova, Smirnov).

(Gorkiy--Automobile industry)

25(1)

PHASE I BOOK EXPLOITATION

SOV/3123

Freydlin, Abram Yakovlevich, Candidate of Technical Sciences

Tekhnika kholodnoy shtampovki; stenogramma doklada (Technique of Cold Stamping; Transcription of a Report) Leningrad, 1958.  
48 p. 6,200 copies printed.

Sponsoring Agencies: Obshchestvo po rasprostraneniyu politicheskikh i nauchnykh znaniy RSFSR, Leningradskiy dom nauchno-tehnicheskoy propagandy; and Nauchno-tehnicheskoye obshchestvo priborostroitel'noy promyshlennosti. Sektsiya kuznetsov i shtampovshchikov.

Ed.: M. I. Sverdlov, Candidate of Technical Sciences; Tech. Ed.:  
M. M. Kubneva.

PURPOSE: The book is intended for foremen and skilled workers in cold-stamping departments.

COVERAGE: This booklet deals with the development of cold-stamping equipment in recent years and problems connected with the design.

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Technique of Cold Stamping (Cont.)

SOV/3123

of dies and cold-stamping operations. The author describes types, designs, and operation of cold-stamping processes. No personalities are mentioned. There are 39 references: 19 Soviet, 14 English, 5 German, and 1 French.

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Ch. I. Presses for Cold Stamping	3
Gap-frame presses	3
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Technique of Cold Stamping (Cont.)

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Ch. II. Cold-stamping Processes  
Economical layout of material

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AVAILABLE: Library of Congress (TJ1450.F7)

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VK/os  
3/16/60

FRYDIN, A. Ya.

25(1,5)

PHASE I BOOK EXPLOITATION

SOV/2294

CIA-RDP86-00513R000413620020-3

Moscow. Dom nauchno-tekhnicheskoy propagandy imeni F.E. Dzerzhinskogo  
Novoye v tekhnologii vysokoproizvoditel'noy listovoy shtampovki;  
sbornik trudov konferentsii (New Features in the Methods of  
High-productivity Sheet Metal Stamping; Collection of Confer-  
ence Transactions) Moscow, Mashgiz, 1959. 228 p. 8,000  
copies printed.

Sponsoring Agency: Obshchestvo po rasprostraneniyu politicheskikh i  
nauchnykh znaniy RSFSR.  
Resp. Ed.: V.T. Meshcherin, Doctor of Technical Sciences, Professor;  
Eds.: V.D. Golovlev, Candidate of Technical Sciences, Docent, and  
Ye.N. Lansko, Candidate of Technical Sciences, Docent; Ed. of  
Publishing House: G.N. Sokolev; Tech. Ed.: B.I. Model';  
Managing Ed. for Literature on Heavy Machine Building (Mashgiz):  
S.Ya. Golovin, Engineer.

PURPOSE: This collection of papers is intended for engineers and  
technicians in sheet metal stamping. It may also be useful to

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SOV/2294

# New Features (Cont.)

students of vuzes and tekhnikums.

COVERAGE: This collection deals with the design and features of some current problems in sheet metal stamping. Also discussed are processing methods still in the experimental stage. Several articles deal with the mechanization and automation of stamping processes and describe recently developed methods, such as explosion forming, the use of automatic rotary transfer lines, and press blocking with the use of radioactive isotopes. No personalities are mentioned. References follow several of the articles.

## TABLE OF CONTENTS:

### Preface

Meshcherin, V.T., [Doctor of Technical Sciences, Professor, Stankoinstrumental'nyy institut, Moskva (Moscow Machine Tool and Instrument Institute)]. Basic Manufacturing Problems of the Near Future

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discusses labor productivity, shapes of work-  
ue, the materials used, stamping operations and techni-  
of production lines, working speed, and the correct meaning  
of basic operational time.

SOV/2294

Pikhtovnikov, R.V. [Doctor of Technical Sciences, Professor, Khar'kovskiy aviatsionnyy institut (Khar'kov Aircraft Institute)]. Use of an Explosive Wave for Drawing and Forming Medium and Large Parts in Small-scale Production

The author discusses experimental fabrication of shallow dish-type parts of an explosive wave caused by gunpowder, gasoline, or natural gas.

22

Koshkin, L.N. [Candidate of Technical Sciences]. New Possibilities in the Development of Sheet Metal Stamping in Connection With the Use of Automatic Rotary Transfer Machines

Mechanical and hydraulic rotary transfer machines are described. The flexibility of these machines allows facility of control, inclusion of chemical and heat treatment in the process, and smooth transition into fully automatic lines.

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# New Features (Cont.)

Freydlin, A.V.  
Gor'kov

New Features (Cont.)

SOV/2294

Konovalova, I.I. [Engineer, Zavod "Metalloizdeliye", Leningrad (Leningrad Metal Products Plant)]. Transfer Machines for Making Safety-razor Blades

206

Fabricating processes and machinery for automatic lines are described, and information on tool life, heat treatment, grinding, and packing of blades is given.

Lanskoy, Ye.N. [Candidate of Technical Sciences, Docent, Moscow Machine Tool and Instrument Institute]. Selection of a Crank Press for Required Force and Work Parameters

217

The author discusses flywheel effect, the meaning of nominal force (capacity), the magnitude of force at various angles of the crank, the work delivered by motor and flywheel, and the work of deformation. Recommendations for selecting the proper press for a given stamping operation are presented.

AVAILABLE: Library of Congress

Card 9/9

GO/ajr  
10-21-59



GUSEV, M.S.; GUSEV, V.M., kandidat tekhnicheskikh nauk, redaktor;  
KAPLAN, M.Ya., redaktor; FRNYDLIN, G.I., inzhener; PUL'KINA, Ye.A.,  
tekhnicheskiiy redaktor.

[Installation of sanitation equipment in residential and civic  
construction] Opyt montazha sanitarno-tekhnicheskikh ustroistv  
v zhilishchnom i grazhdanskom stroitel'stve. Leningrad, Gos. izd-  
vo lit-ry po stroitel'stvu i arkhitekture, 1953. 32 p. (MLRA 7:8)

1. Brigadir santekhnikov Leningradskogo tresta Santekhmontazh.  
(for Gusev, M.S.)  
(Plumbing)

GONCHAROV, F.S., kand.tekhn.nauk; PREYDLIN, G.I., inzh.; SLADKOMEDOV, N.I.,  
inzh.

Asbestos-cement sewage stand pipes for industrial buildings  
and apartment houses. Nov.tekh.mont.i spets.rab.v stroi. 21  
no.9:21-22 S '59. (MIRA 12:11)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut gidrotekhnicheskikh i sanitarno-tekhnicheskikh rabot (for Sladkomedov).  
(Pipe, Asbestos-cement)

ALEKSEYEV, Ye.K., inzh.; IZOUR, R.M., inzh.; LYUBE, Ye.P., inzh.; NIKO-LAYEVSKIY, Ye.Ya., inzh.; PIROGOV, A.N., inzh.; RODIONOVA, R.G., inzh.; TOYBIN, V.A., inzh.; FREYDLIN, G.M., inzh.; KHELYUPINA, A.K., inzh.; CHERNOV, D.L., inzh.; EYDEL'NANT, L.B., inzh.; ZEMUR, N.S., inzh., retsentsent; MOLYUKOV, G.A., inzh., red.; TIKHANOV, A.Ya., tekhn.red.

[Production and installation of pipe systems; reference manual]  
Izgotovlenie i montazh tekhnologicheskikh truboprovodov; spravochnoe posobie. Moskva, Gos.nauchno-tekhn.izd-vo mashinostroit.  
lit-ry, 1960. 574 p. (MIRA 13:7)  
(Pipe fitting)

FEDOSEYEVA Z.K.; FREYDLIN, G.N.

Chemical removal of formic acid from acetic acid with potassium permanganate and bichromate. Khim.prom. no.5:306-307 J1-Ag '56.

1. Yerevanskiy zavod "Polivinilatsetat."  
(Acetic acid) (Formic acid) (Potassium salts)

LOSEV, I.P.; FEDOTOVA, O.Ya.; FREYDLIN, G.N.

Alcoholysis of polyvinyl acetate in presence of polyacids as catalysts. Report No. 1: Study of the rate of reaction. Izv. AN Arm. SSR ser. khim. nauk 10 no.6:403-410 '57. (MIRA 11:6)

1.Yerevanskiy zavod "Polivinilatsetat."  
(Alcoholysis) (Acetic acid) (Chemical reaction, Rate of)

FREYDLIN, G. N., Cand Tech Sci -- (diss) "Alcoholysis of polyvinyl acetate in the presence of a <sup>number</sup> ~~series~~ of cation-exchange resins and sulfo-acids." Mos, 1958. 12 pp (Min of Higher Education USSR, Mos Order of Lenin Chem-Technol Inst im D. I. Mendeleyev), 100 copies (KL, 15-58, 116)

-51-

LOSEV, I.P.; FEDOTOVA, O.Ya.; FREYDLIN, G.N.

Preparation of polyvinyl alcohol by the alcoholysis of polyvinyl acetate in the presence of polyacids as catalysts. Report no.2:

"Life span" of catalysts and feasibility of their regeneration.

Izv. AN Arm. SSR khim. nauk 11 no.1:31-36 '58.

(MIRA 11:6)

1.Yerevanskiy zavod "Polivinilatsetat."

(Acetic acid) (Alcoholysis) (Catalysis)

FREYDLIN, G.N.; ZHENODAROVA, S.M.; CHUKUR, A.P.; FOMINA, N.V.

Vinyl monomers based on dicarboxylic acids. Part 1: Monomers  
of adipic and succinic acids. Zhur.ob.khim. 32 no.3:792-794  
Mr '62. (MIRA 15:3)

(Adipic acid) (Succinic acid)



S/079/62/032/003/003/007  
D204/D302

AUTHORS: Kreydlin, G.N., Zhenodarova, S.M., Fomina, N.V. and Chukur, A.P.

TITLE: Vinyl monomers based on dicarboxylic acids. II. Vinyl alkyl esters of succinic and adipic acids

PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 3, 1962, 795-798

TEXT: Preparation and properties of the above esters was studied owing to the possibility of producing from them internally plasticized polymers. Direct vinylation of monoesters in the liquid phase and the "vinyl exchange" methods were tried. Normal butyl, amyl, hexyl, octyl and nonyl vinyl adipates were synthesised by the catalytic reaction with acetylene in an autoclave, at 160-180°C and 20 atm, over Cd acetate, inhibiting polymerization with hydroquinone. Optimum conditions for this reaction shall be determined in future work. Succinic monoesters were found to be too unstable to be treated in this manner. Vinyl n-R esters (R=methyl to decyl inclusive) of succinic and adipic acids were prepared, in 30-70 and

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S/079/62/032/003/003/007  
D204/D302

Vinyl monomers based on ...

30-97% yields respectively, by the action of vinyl acetate on the corresponding monoester at either 20°C for 5-7 days or 30-40°C for ~ 30 hrs. using Hg acetate/conc. H<sub>2</sub>SO<sub>4</sub> as a catalyst and hydroquinone as an inhibitor. The yields were reduced at higher temperatures. Experimental details are given and physico-chemical properties of the products are tabulated. There are 2 tables and 12 references: 6 Soviet-bloc and 6 non-Soviet-bloc. The 4 most recent references to the English-language publications read as follows: US Pat. 2,472,434, (1949); US Pat. 2,153,987, (1939); W.S. Port in the collection "Industrial Fatty Acids and their Applications", N.Y. (1959); R. Adelman, J.Org. Chem., 14, 1057 (1949).

SUBMITTED: January 30, 1961

Card 2/2

S/080/62/035/005/015/015  
D247/D307

AUTHORS: Freydlin, G. N. and Davydov, V. N.

TITLE: Separation of phthalic acid by esterification without a catalyst

PERIODICAL: Zhurnal prikladnoy khimii, v. 35, no. 5, 1962,  
1150-1153

TEXT: The authors aimed at developing a method of separating iso-phthalic (I) and terephthalic (II) acids, based on selective esterification with MeOH under pressure, to obtain II from a mixture of m- and p-xylenes rather than from the expensive pure p-xylene. The relative rates of esterification varied with temperature, MeOH:acid ratio (n) and time. Thus the rate of esterification of I, at 170 - 180°C and 100 - 200 atm, is 7 - 10 times greater than that of II; raising (n) increased the rate of reaction of II at 180°C (over 1 hr) but not of I. Presence of water retarded both processes to the same extent. The optimum time was 40 - 80 min. The content of II could be raised from 25 - 60% to 87 - 96% by esterification

Card 1/2

FREYDLIN, G.N.; DAVYDOV, V.N.

Separation of terephthalic and isophthalic acids by extraction with  
hot methanol. Zhur.prikl.khim. 35 no.11:2520-2526 N '62. (MIRA 15:12)  
(Terephthalic acid) (Isophthalic acid) (Methanol)

FREYDLIN, G.N.; LITOVCHENKO, N.N.

Imparting water repellent properties to polyvinyl alcohol with  
beta-naphthalenesulfonic acid. Khim.volok. no.2:15-18 '63.  
(MIRA 16:5)

1. Lisichanskiy filial Gosudarstvennogo nauchno-issledovatel'skogo  
i proyektnogo instituta azotnoy promyshlennosti i produktov  
organicheskogo sinteza.

(Vinyl alcohol polymers)  
(Naphthalenesulfonic acid)

L 17480-63 EWP(j)/EWT(m)/BOS ASD PC-4 RM

ACCESSION NR: AP3004760

S/0183/63/000/004/0024/0026

AUTHORS: Freydlin, G. N.; Litovchenko, N. N.; Oshovskaya, G. D. 62

TITLE: Chemical processes occurring in waterproofing with polyvinyl alcohol of Beta-naphthalene sulfonic acid 7

SOURCE: Khimicheskiye volokna, no. 4, 1963, 24-26.

TOPIC TAGS: polyvinyl alcohol, naphthalene, sulfonic acid, waterproofing.

ABSTRACT: Authors investigated the mechanism of the waterproofing method worked out by Freydlin and Litovchenko (Khim. volokna, no. 2, 1963, 15). It was established that the waterproofing is effected by the formation of B-naphthalene sulfonic acid esters of polyvinyl alcohol (PVA). Chemical and X-ray studies indicated that the given method does not cause discernible changes in the crystallinity of the polyvinyl alcohol. "In conclusion we express thanks to V. A. Naumov and V. A. Kachanov (Lisichanskiy filial GIAP) for help and participation in carrying out X-ray analysis and radiometric measurements". Orig. art. has: 1 equation, 1 table and 1 figure.

ASGN: LISICHANSK BRANCH, STATE DESIGN AND PLANNING SCI. RES. INST. FOR THE NITROGEN INDUSTRY.

Card 1/2

L 14948-63

EWJ(j)/EPF(c)/EWT(m)/BDS ASD Pc-4/Pr-4 RM/WW

ACCESSION NR: AP3003790

S/0190/63/005/007/1008/1011

AUTHORS: Freydlin, G. N.; Zhenodarova, S. M.; Fomina, N. V.; Chukur, A. P.

TITLE: Polymerization of vinylalkyl esters of dicarboxylic acids

SOURCE: Vy\*sokomolekulyarny\*ye soyedineniya, v. 5, no. 7, 1963, 1008-1011

TOPIC TAGS: polymerization, vinylalkyl ester, dicarboxylic acid, benzoyl peroxide

ABSTRACT: The polymerization process of vinylalkyl esters of succinic, glutaric, and adipic acids was studied. Experiments were conducted in sealed ampules containing 20 gms of the monomer and 0.1 gm of dissolved benzoyl peroxide in an atmosphere of either nitrogen or air. The ampules were placed in a water bath at temperatures ranging from 65 to 120C, and the progress of the polymerization followed by bromine number determination. It was found that the rate of polymerization increased with the temperature, the yield of the vinylmethylsuccinate polymer at 100C being more than ten times the yield at 80C. In a vacuum the polymerization proceeded at a higher rate and at lower temperatures, while the presence of oxygen delayed it. It was also recorded that the esters of adipic acid polymerize somewhat faster as compared with the esters of succinic and glutaric acid. But it

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L 14948-63

ACCESSION NR: AP3003790

was also found that the induction period of polymer formation increases from vinylmethylsuccinate to vinylhexylsuccinate and practically ceases with the vinylheptylsuccinate ester. Orig. art. has: 1 chart and 4 tables.

ASSOCIATION: Lisichanskiy filial gosudarstvennogo nauchno-issledovatel'skogo i proyektnogo instituta azotnoy promyshlennosti i produktov organicheskogo sinteza (Lisichan Branch of the State Scientific Research and Production Institute of the Nitrogen Industry and Products of Organic Synthesis)

SUBMITTED: 18Dec61

DATE ACQ: 08Aug63

ENCL: 00

SUB CODE: CH

NO REF SOV: 004

OTHER: 004

Card 2/2



*FREYDLIN, G.N.*

S/079/63/033/003/005/005  
A066/A126

AUTHORS: Freydlin, G.N., Zhenodarova, S.M., Chukur, A.P., Pomina, N.V.

TITLE: Vinyl monomers on the basis of dicarboxylic acids. III. Vinyl alkyl esters of glutaric acid. Vinyl cyclohexyl and vinyl benzyl esters of succinic, and adipic acid

PERIODICAL: Zhurnal obshchey khimii, v. 33, no. 3, 1963, 934 - 938

TEXT: The authors describe the synthesis of vinyl alkyl esters of glutaric acid and of normal aliphatic alcohols from methyl to decyl alcohol, as well as the synthesis of vinyl cyclohexyl and vinyl benzyl esters of succinic, and adipic acid. The purpose of the present work was to study the influence exerted by the structure of the substituent in the side chain on the properties of the polymer. The vinyl esters were synthesized as follows: dicarboxylic acid was transformed into a monoester by partial esterification with suitable alcohols. The monoester was subjected to a "vinyl exchange" reaction with the participation of vinyl acetate. The monoalkyl glutarates were found to be very stable, colorless liquids which are able to withstand vacuum distillation. Furthermore, they boil in vacuo at high temperatures.

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Vinyl monomers on the basis of ...

S/079/63/033/003/005/005  
A066/A126

The monocyclohexyl and monobenzyl esters of succinic, glutaric, and adipic acid boil at high temperatures and decompose during distillation. There are 4 tables.

ASSOCIATION: Lisichanskiy filial Gosudarstvennogo instituta azotnoy promyshlennosti i produktov organicheskogo sinteza (Lisichansk Branch of the State Institute for the Nitrogen Industry and for Products of Organic Synthesis)

SUBMITTED: February 27, 1962

Card 2/2

GOLDSTEIN, I.M.; FREYDLIN, G.N.

Hydrolysis of methyl dicarboxylates on KU-2 cation exchangers.  
Zhur. prikl. khim. 37 no.11:2540-2543 N 1964 (MIRA 1964)

FREYDLIN, G.N.; SOLOP, K.A.

Kinetics of the polymerisation of vinyl ester of N,N-diisobutylglutaramide.  
Vysokom. soed. 7 no.6:1060-1064 Je '65. (MIRA 18:9)

1. Filial Gosudarstvennogo instituta azotnoy promyshlennosti, Severodonetsk.

GOL'DENSHTEYN, I.M.; FREYDLIN, G.N.

Hydrolysis of diesters of dicarboxylic acids on the KU-2 cation  
exchanger, Zhur.prikl.khim. 38 no.6:1345-1348 Je '65.

(MIRA 18:10)

FREYDLIN, G.N.; ADAMOV, A.A.; ZAYTSEV, P.M.

Vinyl monomers on a base of dicarboxylic acids. Part 6:  
Direct vinylation of the monoesters of dicarboxylic acids  
with acetylene. Zhur. org. khim. 1 no.4:666-670 Ap '65.  
(MIRA 18:11)

FREIDLIN, G.N.; CHUKUR, A.P.; DZAROKHOKHOVA, L.I.

Vinyl monomers based on dicarboxylic acids. Part 7: Vinyl  
alkyl esters of azelaic and sebacic acids. Zhur. org. khim.  
1 no.8:1367-1369 Ag '65. (MIRA 18:11)

GOL'DENKIN, L.M.; FREYDLIN, G.N.

Hydrolysis of diesters of dicarboxylic acids on ion  
exchangers. Zhur.prikl.khim. 38 no.11:2538-2540 N '65.

Hydrolysis of diesters of carboxylic acids on the  
KU-2 cation exchanger under dynamic conditions.  
Ibid.:2541-2544

(MIRA 18:12)

1. Submitted November 14, 1963.



L 15890-66

ACC NR: AT6004036 EWT(m)/EWP(j)

AUTHOR: Freydlin, G. N.; Adamov, A. A.; Pershenkova, L. A. 08/RM

SOURCE CODE: UR/0000/65/000/000/0037/0040

ORG: Severo-Donetskiy Branch, State Institute of the Nitrogen Industry and Organic Synthesis Products (Severo-Donetskiy filial Gosudarstvennogo instituta azotnoy promyshlennosti i produktov organicheskogo sinteza)

TITLE: Vinyl monomers based on dicarboxylic acids. Part 5: Study of the reaction of vinyl exchange

SOURCE: AN SSSR, Otdeleniye obshchey i tekhnicheskoy khimii. Problemy organicheskogo sinteza (Problems in organic synthesis). Moscow, Izd-vo Nauka, 1965, 37-40

TOPIC TAGS: aliphatic dicarboxylic acid, ester, mercury compound, acetate, organic synthetic process

ABSTRACT: In the synthesis of vinyl methyladipate, the following catalysts of the reaction of vinyl exchange were tested: acetates of copper, zinc, and cadmium, copper chloride, palladium chloride, boron trifluoride etherate, and sulfates of zinc, cadmium, lead, and copper. None of these substances catalyzed this reaction at various temperatures and pressures. When mercury acetate was employed, the reaction time was shortened (equilibrium was reached in less than 24 hr), the

Card 1/2

00513R00041

L 15890-66

ACC NR: AT6004036

reaction rate was accelerated by a rising temperature, high yields of vinyl esters (vinyl stearate, benzoate, oleate, butyrate, methyladipate) were obtained, and no by-products or tars were formed. The vinyl exchange reaction can also be used to synthesize high-boiling vinyl esters. Orig. art. has: 1 figure and 1 table. 3 744

SUB CODE: 07 / SUM DATE: 24Dec63 / ORIG REF: 002 / OTH REF: 003

Card 2/2 *q*

[illegible]

FREYDLIN, I.I.

Use of aminazine for treatment of early tox'coses in pregnancy.  
Vop. okh. mat. i det. 6 no.11:66-68 N '61. (MIRA 14:12)

1. Iz akusherskogo otdeleniya (zav. I.A.Kaplanskiy) Roslavl'skoy  
gorodskoy bol'nitsy (glavnyy vrach G.S.Matviyevskiy)  
(PREGNANCY, COMPLICATIONS OF)  
(CHLORPROMAZINE) (TOXEMIA)

FREYDLIN, I.I.

Use of aminazine in obstetrics. Akush.i gin. no.6:99-100 '61. (MIRA 14:12)  
1. Iz akusherskogo otdeleniya (zav. I.A. Kaplanskiy) Roslavl'-  
skoy gorodskoy bol'nitsy (glavnyy vrach G.S. Matviyevskiy).  
(CHLORPROMAZINE) (PREGNANCY, COMPLICATIONS OF)

FREYDIN, I.L.; MONAKHOVICH, L.S.

Several problems in developing the industry and transportation of the European part of the northern U.S.S.R. Prob. Sev. no.5:19-31 '63.  
(MIRA 16:11)

1. TSentral'nyy ekonomicheskoy nauchno-issledovatel'skiy institut Gosplana RSFSR.

FREYDLIN, I.S.

Structural changes in yeast cells induced by radioactive phosphorus.  
Med.rad. 3 no.4:88-89 J1-Ag '58. (YEAST) (MIRA 12:3)  
(PHOSPHORUS--ISOTOPES)

17(2,12)

SOV/16-59-6-32/46

AUTHOR: Freydlin, I.S.

TITLE: The Antibacterial Action of Extract From Leukocytes of Rabbit Peritoneal Exudate. Author's Summary

PERIODICAL: Zhurnal mikrobiologii, epidemiologii i immunobiologii, 1959, Nr 6, p 125 (USSR)

ABSTRACT: The author studied the antibacterial action of extract from leukocytes of rabbit peritoneal exudate on *Staphylococcus aureus* and *Shigella flexneri* c in vitro. The *Staphylococcus aureus* strains had marked hemolytic and plasma-coagulating properties. The tests showed that extracts prepared from suspensions below a density of 30,000 leukocytes per cu mm had no antibacterial action, whereas extracts from suspensions of 30,000 - 50,000 leukocytes/cu mm had definite antibacterial properties. Extracts from suspensions of 65,000 - 90,000 leukocytes/cu mm prevented the growth of colonies on the liquid nutrient medium. *Shigella flexneri* were more resistant than *Staphylococcus aureus* to the leukocyte extract. In a number of cases *Staphylococcus aureus* strains lost their pathogenicity as a result of contact with the extract. The leukocyte extract proved more effective at 37° than at 4°C. The extracts were also relatively thermo-

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The Antibacterial Action of Extract From Leukocytes of Rabbit Peritoneal Exudate.  
Author's Summary. SOV/16-59-6-32/46

stable, withstanding heating up to 65°C for 30 minutes. However, they lost their bactericidal activity after boiling for 10 minutes. Storage of the extract at 15°C for 2 months led to a decrease in its bactericidal activity of 7-8 times. The results showed that the leukocytes of rabbit peritoneal exudate contain an active bactericidal agent which can be liberated from the leukocytes by extraction.

ASSOCIATION: Kafedra mikrobiologii I Leningradskogo meditsinskogo instituta imeni Pavlova (Department of Microbiology at the Leningrad No I Medical Institute imeni Pavlov)

SUBMITTED: June 27, 1958

Card 2/2

FREIDLIN, I.S.

"D.K. Zabolotnyi (1866-1929)" by I.A.G. Gimmel'farb, K.M. Grodskii;  
in series "Outstanding figures in Russian Medicine." Reviewed by  
I.S. Freidlin. Sov.zdrav. 18 no.4:57-58 '59. (MIRA 12:4)  
(ZABOLOTNYI, DANIIL KIRILLOVICH, 1866-1929)  
(GIMMEL'FARB, I.A.G.) (GRODSKII, K.M.)

FREYDLIN, I.S., vrach (Leningrad)

"Road to health" by I.A.N. Trakhtman. Reviewed by I.S. Freidlin.  
Zdroov'e 6 no.4:32 Ap '60. (MIRA 13:8)  
(HYGIENE) (TRAKHTMAN, I.A.N.)

FREYDLIN, I.S.

Change in the phagocyte activity and some cytochemical reactions of leukocytes in the peritoneal exudate of guinea pigs during the process of immunization. Biul. eksp. biol. i med. 52 no.9:80-83 S '61. (MIRA 15:6)

1. Iz kafedry mikrobiologii (zav. -- prof. V.N. Kosmodamianskiy) I Leningradskogo meditsinskogo instituta imeni I.P. Pavlova. Predstavlena deystvitel'nyy chlenom AMN SSSR H.N. Zhukovym-Verezhnikovym. (PHAGOCYTOSIS) (EXUDATES) (IMMUNITY)

FREYDLIN, I.S.

Phagocytic activity and some cytochemical reactions of leucocytes in peritoneal exudate of guinea pigs following immunization with tetravaccine under conditions of different saturation of the body with vitamin C. Zhur. mikrobiol. epid. i immun. 33 no.10:101-105 0'62 (MIRA 17:4)

1. Iz kafedry mikrobiologii I Leningradskogo meditsinskogo instituta imeni akademika Pavlova.

PROCESSING AND PROPERTIES																									
1ST AND 2ND COLUMNS													3RD AND 4TH COLUMNS												
<p><b>Kinetics of thermal decomposition of potassium formate.</b>  A. A. Balandin, I. Kh. Frekhtin and D. N. Vaskevich.  <i>Sci. Repts. Moscow State Univ.</i> 1936, No. 6, 321-45.  HCOOK (I) yields chiefly K<sub>2</sub>CO<sub>3</sub> (II) at 370-425° and chiefly  K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (III) at 440-475°; both reactions proceed simul-  taneously at 425-440°. The energy of activation of the  former reaction is 10 times that of the latter. The ratio  II/III of the product falls when less than 25% of glass is  added to the I and then rises rapidly to a max. for 10:1  glass-I mixts., at 440°; the ratio is at a min. for 0.8:10  III-I, or 3:10 II-I mixts., at 405°. The process is repre-  sented as 2I → OHCH(OH)COOK(IV) → III + II; IV →  II + CH<sub>2</sub>O; CH<sub>2</sub>O → CO + H<sub>2</sub>. B. C. A.</p>																									
<p>ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION</p>																									
<p>1ST AND 2ND COLUMNS</p>																									
<p>3RD AND 4TH COLUMNS</p>																									

<p>CO</p>		<p>2</p>	
<p>Reaction between sodium formate and sodium hydroxide. A. A. Balandin and L. Kh. Freidlin. <i>J. Gen. Chem.</i> (U. S. S. R.) 6, 808 72(1930). The thermal interaction of alkali salts of monobasic aliphatic acids with caustic alkalis with the formation of hydrocarbons was studied. <math>\text{NaCO}_2\text{H}</math> and <math>\text{NaOH}</math> in various proportions were charged into a 6-cc. ampoule, the top of which was drawn to a delivery tube ending in a capillary and connected with a water-jacketed gas buret. The ampoule was electrically heated in a bath of an equal mixt. of <math>\text{KNO}_3</math> and <math>\text{NaNO}_3</math>. The temp. was kept const. within <math>\pm 0.5^\circ</math> by an elec. regulator. The gaseous and solid reaction products were analyzed (cf. <i>J. Applied Chem.</i> (U. S. S. R.), in press). The reaction begins at <math>210^\circ</math> and proceeds rapidly at <math>230^\circ</math>. The reaction gives pure <math>\text{H}_2</math> and no <math>\text{CO}</math>. With <math>\text{NaOH}</math> in an equiv. or higher ratio, the solid reaction product consists of <math>\text{Na}_2\text{CO}_3</math>. With <math>\text{NaOH}</math> in less than equiv. amt. in addn. to <math>\text{Na}_2\text{CO}_3</math>, there is formed <math>\text{Na}_2\text{C}_2\text{O}_4</math>, increasing with the decreasing ratio of <math>\text{NaOH}</math> and increasing temp. At temps. below about <math>270^\circ</math> no <math>\text{Na}_2\text{C}_2\text{O}_4</math> is formed regardless of the amt. of <math>\text{NaOH}</math> added. <math>\text{Na}_2\text{C}_2\text{O}_4</math> also reacts with <math>\text{NaOH}</math> with the formation of <math>\text{Na}_2\text{CO}_3</math> and <math>\text{H}_2</math>. The reaction begins at <math>260^\circ</math> and proceeds at an unusually high rate at <math>300^\circ</math>. The probable scheme of decompn. is: (1) <math>\text{NaCO}_2\text{H} + \text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2</math>; (2) <math>2\text{NaCO}_2\text{H} \xrightarrow{\text{NaOH catalyst}} \text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2</math>; (2b) <math>\text{Na}_2\text{C}_2\text{O}_4 + 2\text{NaOH} \rightarrow 2\text{Na}_2\text{CO}_3 + \text{H}_2</math>. The difference between schemes 2 and 1 is that the reaction proceeds in 2 stages with the <math>\text{NaOH}</math> acting as a catalyst in a and as a reacting component in b, with the <math>\text{Na}_2\text{C}_2\text{O}_4</math> as the intermediate product. The results of decompn. of <math>\text{Na}_2\text{C}_2\text{O}_4</math> with <math>\text{NaOH}</math> confirm this supposition. Chas. Blane</p>		<p>ASB-3LA DETALLURGICAL LITERATURE</p>	

Thermal decomposition of lead formate and formic acid on metal lead surface. L. N. Ercolani and T. P. Bulanov. *Bull. acad. sci. U. R. S. S., Chem. sci., math. nat., Ser. chem.* 1937, 555-67 (in English 598). The products as well as the kinetics of the decompn. of Pb formate and HCOOH on Pb were studied. The theory of intermediate salt formation is supported by the similarity of products obtained from the decompn. of HCOOH on Pb and Pb formate on Pb. The catalytic effect of Pb on the decompn. of HCOOH is discussed. The absence of volatile liquid products during the decompn. of HCOOH on surfaces of metallic catalysts is explained by the action of the final products upon the intermediate salt. The results were treated according to Arrhenius' equation for first-order reactions giving the energy of activation. Below 255° the gaseous products of (HCOO)<sub>2</sub>Pb decompn. changed in compn. About 284°, the gaseous compn. was const. and above this temp. range the evolution was so rapid as to invalidate observations. The av. value for the energy of activation from three curves is 20,000 cal./mol. (HCOO)<sub>2</sub>Pb → PbO + CO<sub>2</sub> + CH<sub>4</sub> predominates at 240-340° at first. Later (HCOO)<sub>2</sub>Pb → Pb + 2CO<sub>2</sub> + H<sub>2</sub>

leads at all temps. because of the accumulation of Pb. This is shown by the decreasing value of CO<sub>2</sub>/H<sub>2</sub> with 2 as the limit at 240°. Mannich and Guldman found that 2CH<sub>2</sub>O = HCOOCH<sub>3</sub>, which scheme is accepted. The catalytic decompn. of HCOOH was first studied by Sabatier and Mailhe and later by Adkins and Nissen, who established the correlation between the method of prepn. of AlCl<sub>3</sub> and HCOOH = CO<sub>2</sub> + H<sub>2</sub> or HCOOH = CO + H<sub>2</sub>O. Adachew studied the decompn. of HCOOH on charcoal impregnated with PbO. The authors agree that exclusively dehydrogenation results with charcoal as PbO catalyst taken separately. PbO pptd. on charcoal catalyzes dehydration mainly, and at 255-325° there is a fourfold increase; 325° marks the peak of this tendency, while the m. p. of Pb is 327°. Solid and molten Pb cause HCOOH = CO<sub>2</sub> + H<sub>2</sub>, for which data obtained by passing HCOOH over powdered Pb yield 32,000 cal/mol as the energy of activation. A film of Pb formate upon Pb is decomn. efficient as a catalyst. Sergius Kobetsch

ASACSLA METALLURGICAL LITERATURE CLASSIFICATION



Production of oxalic acid in the U. S. S. R. L. Kh. Freidlin. *Org. Chem. Ind.* (U. S. S. R.) 3, 681-6 (1937); cf. Balandin and F., *C. A.* 30, 6628<sup>a</sup>.—The object of the addnl. study of the thermal decompn. of  $\text{HCO}_2\text{Na}$  and  $\text{HCO}_2\text{K}$  was to improve the production of oxalic acid.  $\text{HCO}_2\text{Na}$  in the absence of a catalyst in a glass flask is completely decompd., giving nearly equimol. amts. of  $\text{Na}_2\text{C}_2\text{O}_4$  (I) and  $\text{Na}_2\text{CO}_3$  (II) at 33–88°, 91% I and 9% II at 300–400° and 73% I and 27% II at 427°. The I yield is not increased by the use of vacuum. In the presence of  $\text{Fe}_2\text{O}_3$  (Fe reaction chamber) the yield of I is decreased and that of II increased. Since Cu and CuO do not affect the reaction, the use of Cu reaction chambers may prove to be practical. Moderate amts. of II, such as are present in the cum.  $\text{HCO}_2\text{Na}$  or are formed in the reaction, are not harmful. However, when II is present in excess of 30% the yields of I are greatly reduced. At the optimum temp. of 455°  $\text{HCO}_2\text{K}$  gives 82% I, 18.2% II and gases ( $\text{CO} + \text{H}_2$ ). The reaction temp. can be considerably reduced and the I yield increased to 92–94% from  $\text{HCO}_2\text{Na}$  and 93% from  $\text{HCO}_2\text{K}$  in the presence of catalysts, such as 1,2,4,6- $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{V}_2\text{O}_5$ ,  $\text{EtONa}$ , etc. Chas. Blanc

ASD-5LA METALLURGICAL LITERATURE CLASSIFICATION

The kinetics of the thermal decomposition of potassium formate in the presence of alkali metals. L. Kh. Freidlin, *J. Gen. Chem.* (U. S. S. R.) 7, 1075 (1977). The decompn. of  $\text{HCO}_2\text{K}$  to  $(\text{CO}_2\text{K})_2$  is catalyzed by K or Na and goes completely at 170-220°. A film of oxide on the metal slows the reaction, but amalgams work as well as the free metals. Li and Ca are not good catalysts. The reaction is of the second order and probably goes through the intermediate formation of  $\text{HC(OH)(OK)}_2$ . The energy of activation is 19,170 cal. per mol.

H. M. Lerner

ASH S.L.A. METALLURGICAL LITERATURE CLASSIFICATION

Thermal conversion of potassium and sodium formate in the presence of alkalis. I. A. Podgorny and A. I. Lelchukova. *J. Applied Chem.* (U.S.S.R.) 10, 1089 (1954) (in French 1954) (1957). -- The expts. were carried out in a vertical elec. furnace provided with a temp. regulator.  $\text{HCO}_2\text{Na}$  at 210-230° and  $\text{HCO}_2\text{K}$  at 220-240° did not yield any oxalate at all, independently of the amt. of alkali used; this is the carbonate-formation zone. Above these zones the formates are catalytically converted into oxalate, and this conversion proceeds within a narrow temp. interval (10-20°). At this zone the following

reactions are competing: (1)  $2 \text{HCO}_2\text{M} \xrightarrow{\text{MOH}} \text{M}_2\text{C}_2\text{O}_4$  +  $\text{H}_2$ ; (2)  $\text{HCO}_2\text{M} + \text{MOH} \xrightarrow{\text{catalyst}} \text{M}_2\text{C}_2\text{O}_4 + 2 \text{MOH} = 2 \text{MCO}_2 + \text{H}_2$ . If the alkali concn is low the reaction velocity between formate and alkali is still low even at a high temp. of the catalytic zone; in this case reaction (1) has the highest velocity and the alkali is the true catalyst of the reaction. If the alkali is taken in excess all 3 reactions are equally possible, and the alkali is a catalyst and component of the reaction, although the final product is carbonate. For the prepn. of oxalate, the use of  $\text{HCO}_2\text{Na}$  as a raw material is more advantageous than  $\text{HCO}_2\text{K}$ . Ten references.

A. A. Podgorny

ASD-51.4 METALLURGICAL LITERATURE CLASSIFICATION

10

CH

SELECTIVE ACTION OF THE CATALYSTS ON THE TRANSFORMATION OF FORMIC ACID INTO CARBONATES

1. K. L. Farkhin, *Tr. Akad. Nauk SSSR*, 1975, 11, 975 (Chem. Abstr. 1976, 72, 1051). The previously described method was used. The influence of catalysts typical for ketonization, dehydrogenation and condensation reactions on the direction of the decomposition of Na, K and NH<sub>4</sub> formates was investigated. ThO<sub>2</sub> (selectively) promoted (at 320-340°C) the formation of carbonates from formates, thus, even in the presence of 4% (mol) of ThO<sub>2</sub>, 77.0% of formate was transformed into a carbonate and only 21.2% into an oxalate; in the presence of 10% (and more) of ThO<sub>2</sub>, all formate was transformed into carbonate regardless of the temp. The formation of oxalate was promoted (at 362°C) in the presence of 0.24 mol. of Cu (powdered) per 0.1397 g. of HCO<sub>2</sub>Na, yielding 68.0% of oxalate and 31.3% of carbonate, but further increase of the amt. of catalyst decreased the yield of oxalate and increased that of carbonate. An especially active catalyst for the formation of oxalate was NaNH<sub>2</sub>, in the presence of 2.4% of which 80% of HCO<sub>2</sub>Na was transformed into oxalate at 240°C; therefore, NaNH<sub>2</sub> was as active as alkali metals but absolutely safe to handle. In the presence of alkali metals, NaNH<sub>2</sub> yielded besides HCONH<sub>2</sub>, also 6% of oxalate. Right literature and 4 patent references. A. A. P.

ASH & A METALLURGICAL LITERATURE CLASSIFICATION

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Interaction of sodamide with salts of formic acid. I. H. FAINMAN and A. I. LEONOVA (Compt. rend. Acad. Sci. U.R.S.S., 1969, 19, 701-703).--  
 $\text{NaNH}_2$  catalyzes the reaction  $2\text{HCO}_2\text{X} \rightarrow \text{X}_2\text{C}_2\text{O}_4 + \text{H}_2$  ( $\text{X} = \text{Li, NH}_4, \text{Ca, Zn, Cu, Mn, Ni}$ ) more effectively than  $\text{KOH}$ . As the amount of  $\text{NaNH}_2$  increases the yield of oxalate decreases and the reaction proceeds according to the equation  $2\text{HCO}_2\text{X} + 2\text{NaNH}_2 \rightarrow \text{X}_2\text{C}_2\text{O}_4 + \text{NaOH} + 2\text{H}_2$ . The reactions are exothermic and proceed immediately on addition of the  $\text{NaNH}_2$  to the molten formate. P. J. L.

ASM 3.4 METALLURGICAL LITERATURE CLASSIFICATION

COMMON ELEMENTS		PROCESS AND PROPERTIES INDEX	
CA	<p>Kinetics of thermal decomposition of sodium formate.  <i>L. Kh. Makhlin, Sbornik Nauch. Issledovaniy, Rubel Vsesoyuz. Akad. Priblizhnoi Prirodoz. Nauch. 2, 145-57 (1980); Khim. Referat. Zhur. 1980, No. 10, 5; cf. C. A. 33, 10011.</i>—The kinetics of the decomps. of <math>\text{HCOONa}</math> was investigated from the amt. of the sepd. gas in vacuo and under normal pressure in glass vessels. The solid products of the reaction (taking place in 2 directions <math>2\text{HCOONa} = \text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2</math> and <math>2\text{HCOONa} = \text{Na}_2\text{CO}_3 + \text{H}_2 + \text{CO}</math>) were analysed. Nearly equiv. amts. of carbonate and oxalate were obtained at 331-344°. On increase of the temp. to 400° the yield of oxalate first increased, then decreased. The curves of the summary process were of a complex character and cannot be expressed by a simple kinetic equation. Erosion of the walls of the glass vessel was observed during the reaction. Repeated expts. in the same vessel gave different results. The addn. of ground Schott glass increased the velocity of the reaction. The addn. of solid <math>\text{Na}_2\text{CO}_3</math> or <math>\text{Na}_2\text{C}_2\text{O}_4</math> in amts. not exceeding a definite limit, increased the velocity of the reaction in definite stages. It is concluded that the reaction is related to the heterogeneous process on the walls of the vessel and that it is of a chain character. Oxalate and carbonate are formed simultaneously and the reactions are related to the autocatalytic effect of the products of the reaction.</p> <p>W R. Henn</p>	2	
ASB-3LA METALLURGICAL LITERATURE CLASSIFICATION			
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Reaction of sodium amide with aromatic ketones in the molten state. L. Kh. Ferklin and T. P. Bulanova. *J. Gen. Chem. (U.S.S.R.)* 9, 200-201 (1938). Analogous to the reaction between  $\text{NaNH}_2$  (I) and salts of organic acids the aromatic ketones with I in the molten state undergo cleavage of the CO group to give  $\text{NaHCN}$  (II), the corresponding hydrocarbons and probably  $\text{NaOH}$ , according to the equation:  $\text{RCOR}' + 2\text{NaNH}_2 \rightarrow \text{NaHCN} + \text{NaOH} + \text{RH} + \text{R}'\text{H}$ . In addn., considerable C as well as small amts. of  $\text{HCN}$ ,  $\text{NaCN}$ , dicyanodiamide and  $\text{NH}_3$  are formed, probably due to secondary processes. The reaction, strongly exothermic, proceeds vigorously in all cases at temps. below  $150^\circ$  and for the diketones is often very violent. Benzophenone, benzil and benzoin with I at  $95-110^\circ$  give  $\text{C}_6\text{H}_6$ , II and  $\text{NH}_3$ . Fluorenone and phenanthrenequinone give Ph, in addn. to other products. Anthraquinone with I gives a brown, amorphous product, not investigated. John Livak

Lab of Organic Catalysts, Inst. Org. Chem., AS USSR

ASU-5LA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSING AND PREPARATION																									
1. TITLE AND SUBJECT																									
2. AUTHOR																									
3. SOURCE																									
4. SUMMARY																									
5. ABSTRACT																									
6. REFERENCES																									
7. NOTES																									
8. INDEXING																									
9. EVALUATION																									
10. DISTRIBUTION																									
11. OTHER																									
<p>The interaction of sodamide with the salts of organic acids. L. Kh. Freidlin and A. I. Lebedeva. <i>J. Gen. Chem. (U.S.S.R.)</i> 9, 990-1000(1939); cf. C. A. 32, 9049. —NaNH<sub>2</sub> reacts with formates, acetates and oxalates according to the general equation <math>2 RCO_2M + 2 NaNH_2 = NaHCN + M_2CO_3 + NaOH + 2 RH</math>, while with propionates, succinates and benzoates, the presence of N<sub>2</sub> and NH<sub>3</sub> in the products of reaction was observed, which was explained by the secondary reaction: <math>3 NaHCN = 3 NaCN + N_2 + NH_3</math>. The formation of H at the temp. of the reaction above 300° was explained by the secondary reaction: <math>NaNH_2 + NaCN = Na_2CN + H_2</math>. 24 literature and 19 patent references, covering the period 1852-1939. A. A. Podgorny</p>																									
<p>ASAC-SLA METALLURGICAL LITERATURE CLASSIFICATION</p>																									
<p>GROUPS</p>																									



The interaction of sodamide with carbonyl compounds incapable of enolization: 1. Kh. Abdullin, A. I. Labecheva and N. A. Kazantseva, *J. Gen. Chem.* (U. S. S. R.) **9**, 1593-97, (1931), *Chem. Abstr.* **33**, 8339d. - The investigation of the interaction between  $\text{NaNH}_2$  and carboxylic acids and ketones in the absence of a solvent is continued with higher ketones of the aliphatic, aromatic and terpene series. Again the reaction resulted in the formation of  $\text{NaHCN}$ , corresponding hydrocarbons and H. The reaction with the compds. in which the CO group is linked with a metal ( $\text{Fe}(\text{CO})_5$  and  $\text{W}(\text{CO})_6$ ) and with N ( $\text{CO}(\text{NH}_2)_2$ ) and C $_6$ H $_5$ (HNPh) formed  $\text{NaHCN}$  and metal,  $\text{NH}_3$  and  $\text{PhNH}_2$ , resp. The mechanism of the reaction is explained according to the general equations given in earlier papers (*Chem. Abstr.* **32**, 1631f, 1631g). The solid ketones were fused with Na

[illegible]

PROCESS AND PROPERTIES INDEX

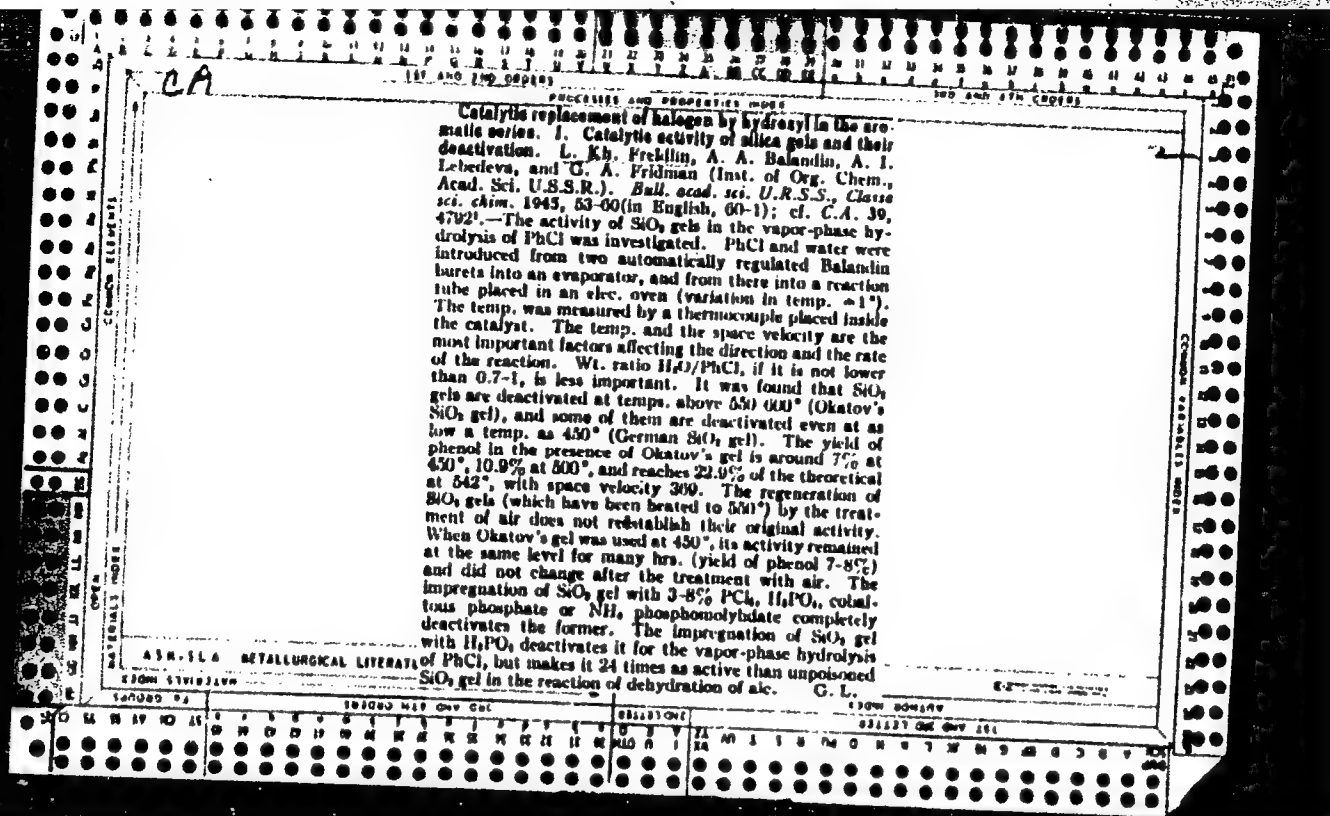
A-1

BC

Thermal transformations of thallous formate. L. C. Freid-  
 lya, A. A. Balashin, and A. I. Lebedeva (*Bull. Acad. Sci.*  
*U.S.S.R., Cl. Sci. Chim.*, 1940, 888-889).—The reactions  
 (I)  $2\text{HCO}_2\text{Ti} \rightarrow \text{Ti}_2\text{CO}_3 + \text{CO} + \text{H}_2$ , (II)  $2\text{HCO}_2\text{Ti} +$   
 $2\text{CO}_2 + \text{H}_2$ , (III)  $2\text{HCO}_2\text{Ti} \rightarrow \text{Ti}_2\text{CO}_3 + \text{CO} + \text{HCO}_2\text{H}$  take place at  
 210–270°; reactions (II) and (III) are favoured by rising  
 temp. and by dehydrogenation catalysts (Pt-black, Or-  
 asbestos). Oxalate is not produced under any conditions.  
 (I) reacts with  $\text{NaNH}_2$  at 97° or  $\text{CaO}$  at 130–230° as follows:  
 $2\text{HCO}_2\text{Ti} + 2\text{NaNH}_2 \rightarrow \text{NaHCN} + \text{NaOH} + \text{Ti}_2\text{CO}_3 + \text{H}_2$ ;  
 $2\text{HCO}_2\text{Ti} + \text{CaO} \rightarrow \text{CaCO}_3 + \text{Ti}_2\text{CO}_3 + \text{H}_2$ , while with  $\text{Ac}_2\text{O}$  at 50°  
 the reaction is  $\text{Ac}_2\text{O} + \text{HCO}_2\text{Ti} \rightarrow \text{TiOAc} + \text{AcOH} + \text{CO}$ .  
 R. T.

METALLURGICAL LITERATURE CLASSIFICATION

E2



Catalytic replacement of halogen by hydroxyl in the aromatic series. II. Activators of silica gel. L. Kh. Fridkin, A. A. Balandin, G. A. Fridman, and A. I. Lebedeva (Inst. Organic Chem., Acad. Sci. U.S.S.R.). <i>Bull. acad. sci. U.S.S.R., Chem. sci. chim.</i> 1945, 375-83 (English summary); cf. preceding abstr.—In the gas-phase exchange reaction between chlorobenzene and water vapor, resulting in the formation of phenol and HCl, it has been variously claimed that alk. earth salts may enhance the activity of the silica gel catalyst. Thorough expl. study of the reaction between 450° and 600° proved this conclusion to be incorrect. The error is ascribed to the use of silica gel catalysts of very low activity. With highly active SiO <sub>2</sub> catalysts, treated with HNO <sub>3</sub> and carefully washed and dried, in quartz or Pyrex reaction tubes 15-20 mm. long, vol. of catalyst 50 ml., temp. const. within ±1°, most inorg. salts were actually found to lower the catalytic activity of SiO <sub>2</sub> gel with regard to the yield of phenol. It is essential to det. the yield of both phenol and HCl, as a substantial yield of HCl coupled with a poor yield of phenol indicates preponderance of side reactions; consideration of the yield of HCl alone has in the past led to erroneous conclusions. A series of runs were made with SiO <sub>2</sub> gel impregnated with various salts, using a total amt. of about 13-17 g. C <sub>6</sub> H <sub>5</sub> Cl in each run and varying amts. of H <sub>2</sub> O, from H <sub>2</sub> O/C <sub>6</sub> H <sub>5</sub> Cl = 0.6 to 0.5. Between runs, the catalyst was regenerated by heating in a stream of air at 500° for 5 hrs. With CuCl <sub>2</sub> (5%) in the catalyst, the activity is lowered in the whole temp. range 450°-550°; at 550°, the yield in phenol is 8-10%, as compared with the 20-22% without salt. Ammonium molybdate (5%) leaves the activity of the SiO <sub>2</sub> gel catalyst practically unchanged. At 450°, HgCl <sub>2</sub> (5%) lowers the activity considerably; the effect disappears at 500° and above, due no doubt to volatilization of the HgCl <sub>2</sub> at higher temp. In the presence of FeCl <sub>3</sub> (5%), no phenol was formed even after 3 hrs.; the yield in HCl was 5-6% of the theory; the catalyst remained white, indicating total inactivity. Lowering of catalytic activity (from 10-12% to 8% yield in phenol) was also observed with MnCl <sub>2</sub> (10%); after regeneration at 500°, the catalyst appears to be entirely inactive with regard to formation of phenol, although it remains somewhat active with respect to HCl. A highly active SiO <sub>2</sub> gel catalyst (phenol yield at 600° up to 44.6% of the theory) became considerably less active when impregnated with BaCl <sub>2</sub> , CaCl <sub>2</sub> , or MgCl <sub>2</sub> (10%); at 600° within about 2 hrs., with 10% BaCl <sub>2</sub> , CaCl <sub>2</sub> , or MgCl <sub>2</sub> , yields of phenol were, resp., 21%, 8.6%, 14.4%, as compared with 44.6% without salt. The only case of pos. activation by addn. of salt is CuCl <sub>2</sub> ; with 2% CuCl <sub>2</sub> , the yield of phenol attained 75% of the theory; Tishchenko's ternary catalyst "DT" contg. 2% CuCl <sub>2</sub> and 10% MgCl <sub>2</sub> gave a yield of 77.5%. The increased activity is entirely due to the presence of CuCl <sub>2</sub> ; the addn. of MgCl <sub>2</sub> resulted in a slight lowering of the specificity of the catalyst. Catalysts rendered inactive by inorg. salts can be fully restored by impregnation with CuCl <sub>2</sub> . N. Thon <td>2</td>		2
<p>ASAC-54 METALLURGICAL LITERATURE CLASSIFICATION</p> <p>FROM SYNONYMS</p> <p>SYNOPSIS</p> <p>EXTRACTS WITH ONLY USE</p> <p>ABSTRACTS</p> <p>EXTRACTS WITH ONLY USE</p>		

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<p>The reactivity of phenyl halides in catalytic vapor-phase hydrolysis. I. Kh. Erekhin, A. A. Balandin, and G. A. Fridman (Inst. Org. Chem., Acad. Sci. U. S. S. R.), <i>Bull. Acad. Sci. U. S. S. R. Chem. Ser. Chem.</i> 1943, 665 (in English, 664).—PhCl and PhBr are catalytically hydrolyzed to PhOH when passed over SiO<sub>2</sub> gel with steam. The yield of PhOH from PhBr is always less than from PhCl, but reaches 8.8% at 550°. Impregnation of the SiO<sub>2</sub> with CuCl<sub>2</sub> increases the hydrolysis of both compounds, but especially of PhBr. PhI is hydrolyzed only slightly, giving a max. yield of PhOH at 400° of 4.3%. The reaction is not catalytic, since the presence of SiO<sub>2</sub> or SiO<sub>2</sub> and CuCl<sub>2</sub> does not increase the yield. PhP is only slightly hydrolyzed. The max. yield of PhOH is 4.2% at 700°, and at 800° this has dropped to 0.6%. SiO<sub>2</sub> does not catalyze this reaction. The variability in the results with different halides is probably due to the acid nature of SiO<sub>2</sub>, which catalyzes the hydrolysis through intermediate formation and hydrolysis of a Ph ester. H. M. Leicester</p>																																																			
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<p>10</p> <p>Mechanism of vapor-phase catalytic substitution by hydroxyl of halogen attached to aryl group. I. Kh. Prekhlis, A. A. Balandin, G. A. Fridman, and A. I. Lebedeva. <i>Bull. Acad. Sci. USSR, Div. Chem.</i> 1943, No. 2, 151 (1944 English, 162). A theory of the vapor-phase hydrolysis of aryl halides, catalyzed in the liquid phase by Cu and in the vapor phase by Sb<sub>2</sub>Se<sub>3</sub>, is advanced. G. Lebedev</p>																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																						
<p>ASB-11.4 METALLURGICAL LITERATURE CLASSIFICATION</p>																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																						

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<p>Hydrolysis of chlorobenzene by water vapor in the presence of silica gel catalysts. L. Kh. Frekhtin, A. A. Balandin, G. A. Fridman, and A. T. Lebedeva. <i>Khimicheskaya Prom.</i> 1945, No. 12, 8-11; cf. C.A. 39, 47921; 40, 46761, 46877. This is a summary of the more important of previous expts. and some new data. In the hydrolysis of PhCl with SiO<sub>2</sub> gel as catalyst any mineral admixts. except Cu and its salts depress the activity of the catalyst and promote side reactions. CrCl<sub>3</sub> lowers the activity of the catalyst considerably, but does not affect its selectivity and facilitates its regeneration. A mixed catalyst of SiO<sub>2</sub> gel, CrCl<sub>3</sub>, and CuCl<sub>2</sub> has the activity of SiO<sub>2</sub> gel-CuCl<sub>2</sub>, is more stable thermally, and is readily regenerated with air at 450°. Fe compds., be they added or derived from the app., poison the catalyst. Washing the SiO<sub>2</sub> gel with HNO<sub>3</sub> increases its catalytic efficiency (cf. D. Tishchenko, et al., C.A. 30, 4155). With a mixed catalyst contg. CrCl<sub>3</sub>, S and CuCl<sub>2</sub>, 0.2% at 820° there were practically no side reactions and at 600° side reactions amounted to 15% of the reacting PhCl. With time the effectiveness of the catalyst declines but after regeneration the original efficiency is somewhat surpassed. The increase of Cu in the catalyst beyond a certain min. does not raise the efficiency of the catalyst. The temp. range of the catalytic activity of the catalyst is 400-600°. PhCl hydrolyzes easier than PhBr. PhI hydrolyzes very slowly and the reaction is not catalyzed by silica gel. PhF did not hydrolyze even at 620°.</p> <p style="text-align: right;">M. Hirsch</p>																																																			
<p>ASH-SLA METALLURGICAL LITERATURE CLASSIFICATION</p>																																																			

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<p>The mechanism of the vapor-phase catalytic substitution of hydroxyl for aryl halogen. L. Kh. Freidlin, A. A. Balandin, A. I. Lebedeva, and O. A. Fridman (Acad. Sci. of U.S.S.R., Moscow). <i>Acta Physicochim. U.R.S.S.</i> 21, 55-78(1946).—The present work on the vapor-phase reaction of aryl halides with <math>H_2O</math> in the temp. range of 400°-600° is compared with past work, particularly in the case of chlorobenzene (I). The unique role of <math>SiO_2</math> gel (II) as a catalyst for the replacement of aryl halogen by <math>OH</math> is pointed out, as well as the fact that only Cu and its salts promote the action of II, whereas other salts decrease it. A theory of the process based on the formation of intermediate silicate esters is proposed which explains the previous facts as well as the other observed phenomena accord. with the vapor-phase hydrolysis of I to phenol.</p> <p>P. I. Fivine</p>																																																			
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PROCESSES AND PROPERTIES

Conversion of aryl halides and elimination of aromatically bound halogen by water vapor. L. Kh. Fridlin, A. A. Balandin, A. I. Lebedeva, and G. A. Fridman. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1946, 439-46. —A new direction of the reaction of  $ArX$  with steam was found; this results in elimination of the halogen (replacement by H) and is catalyzed by  $CuCl_2$  deposited on oxides of Ti or Sn. Only 2-3%  $PhOH$  is formed, while the gas effluent contains  $HCl$ ,  $CO$ ,  $CO_2$ ,  $Cl_2$ ,  $O_2$ , and  $H_2$  are absent. It is believed that the initial reaction is an oxidation:  $PhCl + 6H_2O \rightarrow HCl + 6CO + 8H_2$ ;  $CO$  is then oxidized by  $H_2O$  to  $CO_2$ , while  $H_2$  reacts with  $PhCl$  and gives  $HCl$  and  $C_6H_6$ .  $Cl_2$  is eliminated more readily than  $Br_2$ , while dichlorobenzenes give a stepwise reaction yielding  $C_6H_5Cl$  and  $PhCl$ . Passage of 10.0 g.  $PhCl$  and 13.8-18 g.  $H_2O$  over  $TiO_2$  contg. 6%  $CuCl_2$  at  $500^\circ$  with a space velocity of 134-281 gave 1.0-2.7%  $PhOH$  and 10.1-54.9%  $HCl$ ; a similar catalyst based on  $SnO_2$  gave 0.7-1.0%  $PhOH$  and 18-32%  $HCl$ . Either  $TiO_2$ ,  $SnO_2$ , or  $Cu$  alone are poorly active. The yields of benzene range about 55% at  $500^\circ$ , with noticeable drop at lower temps., using the combination catalysts (no detailed yields of  $C_6H_6$  are given). The catalyst slowly loses its activity and must be regenerated by air blowing at  $500^\circ$  and satn. with  $CuCl_2$ . The "elimination" reaction begins at about  $400^\circ$  on the combined catalysts. A  $TiO_2-CuCl_2$  catalyst used at  $500-550^\circ$  with  $PhBr$  and  $1-CuCl_2$  gave similar results: very little  $ROH$  forms, while  $PhBr$  reacts some 20% less than  $PhCl$  under comparable conditions;  $1-CuCl_2$  gives about 40% smaller yields than are obtained from  $PhCl$ . Passage of a 1:1 mixt. (by wt.) of  $COCl_2$

$Cl_2C_6H_5$  and  $H_2O$  over  $TiO_2-CuCl_2$  at  $500^\circ$  with a space velocity 307-307 gave 52%  $HCl$ , and the products contained  $PhCl$  and  $C_6H_6$  in a 6:1 ratio. Passage at  $500^\circ$  of 23.8 g.  $PhCl$  and 3.5 l.  $H_2$  in 115 min. (space velocity 242) over the  $TiO_2-CuCl_2$  catalyst gave 60%  $HCl$ ; similar passage of  $PhCl$  mixed with 1.3 parts  $H_2O$  gave only 25%  $HCl$ ; this confirmed the theory of the process given above, showing that  $H_2$  liberated by catalysts is capable of complicating the usual aryl halide catalytic hydrolysis. Obviously, catalysts suitable for this "elimination" reaction are undesirable for the conversion of aryl halides into phenols.

G. M. Kozlovskii

<p>CA</p> <p>10</p> <p>Inat. Org. Chem., AS USSR</p>	
<p>PROCESSES AND PROPERTIES INDEX</p> <p>Catalytic exchange of halogen for hydroxyl in the aromatic series. III. Activating effect of copper. L. Kh. Pridlin, A. A. Balandin, A. I. Lebedeva, and G. A. Fridman. <i>Bull. acad. sci. U.R.S.S., Classe III. chim.</i> 1947, 515-22 (in Russian); cf. <i>C.A.</i> 40, 4577; 30, 4792; 40, 5027. —The catalytic activity of silica gel in the gas-phase conversion of PhCl into PhOH by H<sub>2</sub>O vapor is strongly increased by Cu. The catalyst is prepd. by impregnation of silica gel with 0.2% CuCl<sub>2</sub> and admixt. of metallic Cu (5%) to compensate for loss of Cu through volatilization, which is noticeable above 400° and marked above 450-500°. With metallic Cu added, the activity of the catalyst is fully preserved up to 550° but falls off somewhat on heating above that temp.; pure silica gel suffers thermal deactivation in about the same temp. range (500-550°). In tubes of 15-20 mm. diam., vol. of catalyst 50 ml., with 10.0 g. PhCl and about 10-15 g. H<sub>2</sub>O passed in each run, at 450°, 500°, 550°, and 600°, 40-80 min., the yields of PhOH were approx. twice those obtained with the same catalyst without Cu. Complete regeneration is achieved by heating in an air stream 0 hrs. at 500°. Yields of PhOH attained, were over 50% of the PhCl passed. Catalysts poisoned by H<sub>3</sub>PO<sub>4</sub>, MgCl<sub>2</sub>, or CuCl<sub>2</sub> can be almost completely restored by impregnation with CuCl<sub>2</sub> but Cu is without effect on thermally deactivated catalysts. Thus, treatment with Cu salts can be used to distinguish between reversible and irreversible deactivation. Activation with CuSO<sub>4</sub> is equally effective, CuCl<sub>2</sub> being formed in the course of the reaction. Cu alone does not catalyze the exchange. N. Thon</p>	
<p>ASS-5LA METALLURGICAL LITERATURE CLASSIFICATION</p>	

HEYMARK, I.W.; FRYDLIN, L.Kh.; FRIDMAN, G.A.; SHYNFAYN, R.Yu.

Structural changes of a silica-gel catalyst during its poisoning.  
Dop.AN URSR no.5:27-32 '49. (MLRA 9:9)

1. Institut fizichnoi khimii imeni L.V.Pisarshevs'kogo AN URSR i  
Institut organichnoi khimii AN URSR. Predstaviv diyaniy chlen AN  
URSR O.I.Brods'kiy.  
(Catalysts) (Silica)

CA

Rupture of the ether bond in phenol ethers. II. Catalytic decomposition of anisole and phenetole. L. Kh. Freidlin, A. A. Balandin, and N. M. Nazarova. *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1949, 108-201; *ibid.*, 43, 575-61. In uncatalyzed low-temp. pyrolysis of PhOMe and PhOEt (in the temp. range of 482-707° and 440-610°, resp.), in glass tubes, the primary step,  $\text{PhOR} \rightarrow \text{PhOH} + \text{R}^\cdot$  where R $^\cdot$  is an alkylidene radical,  $\text{PhOR} \rightarrow \text{PhOH} + \text{R}^\cdot$  is followed by  $\text{R}^\cdot + \text{PhOH} \rightarrow \text{RC}_6\text{H}_5\text{OH}$ , and accompanied by a side reaction of the rearrangement type,  $\text{PhOMe} \rightarrow \text{PhCH}_2\text{OH}$ , the latter giving, on further decomposition, BzH and CO. The max. yields of PhOH, from PhOMe and PhOEt, are 51.7 and 60.2%, at 440° and at 574°, resp. They fall with further rising temp. These yields can be substantially improved only if the reactions are conducted at lower temps. in the presence of catalysts. No PhOH was obtained from PhOMe at 443° on silica gel in the absence of H<sub>2</sub>O. With mixts., PhOMe + H<sub>2</sub>O (1:1 or 2:1 by wt.), at 574° and 607°, space velocity approx. 300 g./l. catalyst/hr., the yields were 34 and 48%, resp. (relative to the PhOH passed) i.e. of the same order as in glass tubes, and 24% at 647°; in both cases, H<sub>2</sub>O only promotes the pyrolysis, but does not react, as evidenced by the absence of products of hydrolysis (MeOH). In contrast to glass and to silica gel, active silicates catalyze the pyrolysis efficiently. With PhOMe (without H<sub>2</sub>O), at a space velocity ~300 g./l. catalyst/hr., in 40-min. runs, at 282, 346, 410, 443, and 482°, the yields of PhOH were 17.0, 53.7, 75.2 (max.), 66.4, and 53.3%. Decomposition begins about 250° lower than in the uncatalyzed reaction, and is max. at 410°, whereas without catalyst there is no reaction yet at 443°. In the presence of a catalyst, no gas is evolved at 443°, and only 400 ml. gas is evolved from 9.64 g. PhOMe at 482° (CH<sub>4</sub>, CO, and H<sub>2</sub>, no unatd.). The catalyzate contains PhOH and cresols, but no BzH and no PhCH<sub>2</sub>OH; consequently, the isomerization reaction

which takes place as a side reaction in uncatalyzed pyrolysis is suppressed. H<sub>2</sub>O vapor lowers the yields of PhOH, e.g., at 440°, H<sub>2</sub>O:PhOMe = 0.9:1 (by wt.), PhOH = 25%, and, at 443°, H<sub>2</sub>O:PhOMe = 0.5:1, PhOH = 31%. This neg. effect of H<sub>2</sub>O is ascribed to screening of active centers, and indicates absence of a hydrolytic reaction between PhOMe and H<sub>2</sub>O. The activity of the catalyst can be fully restored by treatment with air at 550-75°. The yield of PhOH from PhOEt is 50.2% at 557°, and is max., 81.2%, at 346°. The amt. of gas evolved is less than in uncatalyzed pyrolysis, but it contains more C<sub>6</sub>H<sub>6</sub> (83.1% at 381°). The liquid catalyzate contains PhOH and alkylphenols, no BzH. The yields of PhOH are decreased in the presence of H<sub>2</sub>O. N. Thon

Cataltic replacement of halogen by hydroxyl in the aromatic ring. IV. Vapor-phase hydrolysis of *o*- and *p*-chlorophenols and *o*- and *p*-dichlorobenzenes. I. Kh. Preidlun and G. A. Fridman (Acad. Sci., U.S.S.R., *Izvit. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1949, 317-25; cf. *C.A.* 39, 4792; 40, 4576; 42, 2211d, 6333d).—Hydrolysis of *p*-ClC<sub>6</sub>H<sub>4</sub>OH at 500° over porcelain chips gave no HCl or hydroquinone; over silica gel a conversion of 16% was reached, and 4.6% hydroquinone isolated; silica gel promoted by CuCl<sub>2</sub> gave 4.5% hydroquinone at 450° and 12% at 550°, based on the amt. of ClC<sub>6</sub>H<sub>4</sub>OH introduced; the latter figure corresponds to 32% conversion; the yield of HCl always exceeded that of hydroquinone; traces of resorcinol (up to 1.2%) were also detected. The high yield of HCl is caused by the dehydrohalogenative action of the Cu promoter, as omission of H<sub>2</sub>O at 600° gave 23% PhOH. *o*-ClC<sub>6</sub>H<sub>4</sub>OH over silica promoted by CuCl<sub>2</sub> gave a max. yield of HCl (33%) at 550° (16.8% at 450°), but the pyrocatechol yield was low: 3.9% at 450° and 3.4% at 550°. *o*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> over silica gel gave 1-2% pyrocatechol and 0-1.7% *o*-ClC<sub>6</sub>H<sub>4</sub>OH at 600°; at 550° the values are 1.4 and 4.5%, resp., while at 450° they are 0.7 and 5.4%; here again HCl evolution is well ahead of hydrolysis; promotion by CuCl<sub>2</sub> does not affect the pyrocatechol yields but increases the ClC<sub>6</sub>H<sub>4</sub>OH yields by 300-400%, with a 200-300% increase of HCl evolution. *p*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> over silica promoted by CuCl<sub>2</sub> gave a max. yield of 4.6% hydroquinone at 600°; the ClC<sub>6</sub>H<sub>4</sub>OH yield also rises with temp. and reaches 41% of converted product at 600°; total conversion, judged by HCl evolution, is max. (30.9%) at 600°. The *p*-derivs. are hydrolyzed more readily than *o*-derivs.

G. M. Kosolapoff

CA  
 Cleavage of the ether link in simple ethers of phenol.  
 I. Low-temperature decomposition of anisole and phen-  
 tole in sealed tubes. L. Kh. Freidlin, A. A. Balandin,

and N. M. Nazarova. *Izvest. Akad. Nauk S.S.S.R.,  
 Otdel. Khim. Nauk* 1949, No. 1, 102-9.—Thermal de-  
 composit. of PhOMe and PhOEt proceeds primarily with  
 formation of PhOH, with probable formation of free alkyl  
 radicals. Simultaneously the ethers undergo a "carbino-  
 type" rearrangement into aralkyl alcs. The free radicals  
 from the 1st reaction lead to formation of alkylphenols.  
 Water vapor does not alter the products of the reaction but  
 decreases the reaction rate. Vapors of PhOR were  
 passed through a Pyrex tube, packed with glass fragments,  
 and heated to 482-707° for PhOMe or 440-640° for PhOEt;  
 PhOH was estd. in the effluent bromometrically, while the  
 other products were isolated by fractionation. PhOMe  
 yields 14% PhOH at 521° at space velocity 812 in an  
 empty tube; the packed tube gave the following results  
 (in the above order): 11.2%, 682°, 287; 22.8%, 521°,  
 289; 45.1%, 574°, 297; 51.7%, 640°, 287; 45.9%, 707°,  
 297. The off-gas ranged from 0.7 to 2.5 l. (from 14.85 g.  
 PhOMe), parallel with the PhOH yields; the remaining  
 material on distn. yielded C<sub>11</sub>H<sub>8</sub>, PhMe, unreacted PhOMe,

and BzH; the ratio of PhOH to C<sub>11</sub>H<sub>8</sub> was 13:1; the off-  
 gas was free of C<sub>11</sub>H<sub>8</sub> and contained CO, CH<sub>4</sub>, and H<sub>2</sub>.  
 Addn. of steam to the feed (1.0-1.2 ratio) at 501-674° gave  
 somewhat lower yields of PhOH at higher space velocities,  
 but approx. the same as above at low space velocity (145).  
 PhOEt is decomposed at lower temps. and appreciable reac-  
 tion occurs at 440° (5.8% PhOH); the best yield (10.2%)  
 occurs at 574° at space velocity 252. The off-gas contains  
 but 10% C<sub>11</sub>H<sub>8</sub> (the rest is as given above); the effluent  
 contains alkylphenols (not isolated nor characterized),  
 C<sub>11</sub>H<sub>8</sub>, and unreacted PhOEt; no PhMe or BzH was found.

G. M. Kosolapoff

ASAC-11A METALLURGICAL LITERATURE CLASSIFICATION

CA

2

Relation between the type of the porosity of a silica gel and its catalytic properties. I. Kh. Fridlin, I. R. Nelmark, G. A. Fridman, R. Yu. Shestifan and P. I. Khutsev (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1950, 521-30.—The fact that vapor-phase hydrolysis of aryl halides is catalyzed by the typically hydrophilic catalyst silica gel proves that the activation bears on the  $H_2O$ ; a typical activator of aryl halide,  $Cu$ , does not catalyze the reaction. Only non-hydrated silica gel is active; consequently, the active centers lie at the OH groups of the silica gel. However, the catalytic activity of a silica gel is governed not only by the d. of these centers but by the vol. of the micropores, which det. the sp. surface area, and the amt. of intermediate pores necessary for the transport of reactants and products. Yields of  $PhOH$  and of  $HCl$  from  $PhCl$  and  $H_2O$  passed in approx. equal amts., at  $\sim 300$  g./l. catalyst/hr., in 110-min. (11 g.  $PhCl$ ) runs at increasing temps. from 450 to 650°, with air-stream regeneration at 525° between runs, were detd. for 6 types of silica gel catalysts with the following characteristics (total pore vol., micropore vol. (ml./g.), vol. of absorbed liquid  $C_6H_6$  at the atm. pressure, vol. of intermediate pores (ml./g.), Brunauer-Emmett-Teller sp. surface area in sq. m./g.): (I) 0.60, 0.32, 0.60, 0.39, 300; (II) 0.40, 0.26, 0.45, 0.19, 450; (III) 0.45, 0.32, 0.44, 0.14, 500; (IV) 1.33, 0.35, 1.19, 0.94, 490; (V) 0.93, 0.23, 0.95, 0.72, 420; (VI) 0.93, 0.18, 0.94, 0.76, 325. Curves of the yield of  $PhOH$  (in %) against the temp. are of 3 types: Catalysts I, IV, and V have a distinct max. at about 600°; the subsequent fall of the rate is due to irreversible thermal deactivation. This is most marked with catalyst I which has the smallest vol. of intermediate pores. The 2nd type is represented by II and III. Catalyst II has a low activity, practically independent of the temp. between 450 and 650°.

III has a temp.-independent activity between 550 and 600°, followed by a fall. Absence of an increase of the activity with the temp. in the case of II is attributed to the insufficiency of intermediate pores, i.e. to inadequate diffusion. This same factor is responsible for the relatively not very high activity of III, despite its very high microporosity. The 3rd type, represented by catalyst VI, characterized by a small micropore and a large intermediate-pore vol., is an S-shaped curve with the yield steadily increasing with temp. up to 650°. The selectivity of the catalysts, characterized by the yield ratio  $HCl/PhOH$ , is different for the 3 types. It is lowest with silica gels II and III, with the  $HCl/PhOH$  yield ratio increasing very strongly with the temp., from about 550° and 600° on, resp. With the gels I, IV, and V, the ratio begins to increase with the temp. from 600° on, with VI, it remains very nearly temp. independent,  $\sim 1$ . The thermal stability, expressed by the ratio of the  $PhOH$  yields at 600 and 650°, decreases in the order VI (0.8), V (1.1), IV (1.4), I and III (2.4), i.e. the least microporous VI is the most thermostable; catalysts I and III, having the smallest vol. of intermediate pores, are the least stable. Catalyst II is not included in this evaluation on account of the predominant role of inhibited diffusion. An impure silica gel, found to be very highly active at 450°, but almost completely inactivated at 550°, was found to be very highly microporous, and, by the reversibility of its  $MeOH$ -vapor adsorption curve, almost completely devoid of intermediate pores, which accounts for its exceptionally poor thermal stability.

N. Tsou

1951

CA

2

Promotion of nickel catalyst by hydrogen. L. Kb. Freidlin and N. I. Ziminova. *Izvest. Akad. Nauk S.S.S.R., Khim. Nauk* 1980, 650-61. — Studies on inactivity of pure degassed films of Ni as catalysts were continued (Roginskii, C.A. 36, 329). Leaching of  $\text{Al}_2\text{Ni}_3$  2 hrs. at  $105^\circ$  with NaOH, followed by washing with  $\text{H}_2\text{O}$ , EtOH, and toluene gave the basic catalyst contg. 2.33 g. Ni per ml. After satn. with H for 10 min., residual H was displaced with

N and the unsatd. compd. was introduced; thus hydrogenation was caused at the expense only of H retained by the catalyst. After washing with toluene the operations were repeated.  $\text{PhNO}_2$ ,  $\text{CH}_2\text{CHOH}$ , etc., were most satisfactory for the removal of the retained (adsorbed) H from the catalyst. Removal of as much as 210 ml. adsorbed H from 2.33 g. Ni still leaves certain activity (hydrogenating) in the catalyst, and the latter is pyrophoric; but removal of 223-4 ml. H (24-hr. contact of the unsatd. compd.) completely inactivates the catalyst, which is then nonpyrophoric. The removal of H is speeded by higher temp., and at  $60^\circ$  the max. amt. of H removable from 2.33 g. Ni is about 224 ml., and only with removal of the last 3-4 ml. does the activity vanish. Thus, skeletal Ni is a catalyst that is promoted by adsorbed H; possibly other forms of Ni catalyst are similarly promoted. Some substances (undescribed) on hydrogenation over Ni lead to complete poisoning of the catalyst, which illustrates a case of the poison being either the reacting substance itself or an intermediate that reacts with the promoter. G. M. Kosolapoff



CA

A piston device for regular feeding of liquids. A. M. Levit and L. Kh. Freidlin (Acad. Sci. U.S.S.R., Moscow) *Zavodskaya Lab.* 16, 244-5 (1950).--The app. is a pressure-operated buret or syringe, the plunger of which carries a substantial wt., which is uniformly lowered by means of clockwork. G. M. Kinsolapoff.

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CA

" Differentiated outgassing of nickel. Two forms of binding of hydrogen in a catalyst. L. Kh. Freidlin and N. I. Zimkhova (Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 74, 955-8 (1980). -- Differentiation between the H<sub>2</sub> adsorbed on and the H<sub>2</sub> dissolved in H<sub>2</sub>-saturated Ni was realized, and the nonequivalence of the 2 forms of H<sub>2</sub> was demonstrated by expts. of hydrogenation of org. compds. with the H<sub>2</sub> contained in Ni. The org. compds. were hydrogenated, in a N<sub>2</sub> atm., with Ni satd. with H<sub>2</sub> for 10 min. prior to the expt. The compds. investigated fell into 3 groups: Group I, represented by Michler's ketone, withdraws from the Ni only a definite fraction of its H<sub>2</sub> content. Thus, 2.33 g. Ni gave up a total of 49-50 ml. H<sub>2</sub>. On subsequent matn. with H<sub>2</sub>, that amt. of Ni takes up exactly the

same amt. of H<sub>2</sub> as given up in the hydrogenation, and the process can be alternated repeatedly, with the amts. of H<sub>2</sub> given up and taken up again remaining the same. That 49-50 ml. H<sub>2</sub> is evidently the adsorbed H<sub>2</sub>. With substances of group II, represented by styrene, cinnamic acid, or its esters, the 2.33 g. of Ni gives up 198-200 ml. H<sub>2</sub>, and, on subsequent matn., takes up only 19-21 ml. If now the Ni is treated with a compd. of group I, it will give up only those 19-21 ml. Consequently, compds. of group II withdraw from the Ni, in addn. to the adsorbed H<sub>2</sub>, also part of the dissolved H<sub>2</sub>, with a concomitant partial deactivation of the adsorptive capacity of the Ni, i.e. partial destruction of its active centers. Substances of group III, e.g. PhNO<sub>2</sub> and vinyl butyl ether, withdraw the total amt. of both the H<sub>2</sub> adsorbed and that dissolved in the Ni; the amts. withdrawn from 2.33 g. Ni by different compds. of that group were very close, 219-220, 220-222, and 223-224 ml. This is also the total amt. of H<sub>2</sub> that can be withdrawn from 2.33 g. of Ni by first treating it with a compd. of group I and then, after washing with toluene, by a substance of group III. After removal of all the H<sub>2</sub>, the Ni becomes inactive for the hydrogenation of compds. of group I. The H<sub>2</sub> adsorbed on the surface evidently forms no part of the active centers. In the Ni sample investigated, the ratio H (adsorbed):H (dissolved):Ni = 2.7:10, i.e. the sample contains 1 atom of dissolved H per 2.7 atoms Ni. This coincides with the ratio H:Ni = 1:3 arrived at by Davison and Germer (C.A. 22, 350) by electron diffraction. The no. of H atoms dissolved in Ni is about 3.5 times the no. of H atoms adsorbed; i.e., the no. of potentially possible active centers is 3.5 times the no. of actual centers. The no. of the latter is roughly 1/3 the no. of Ni atoms. N. Thon

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**B**

**R133\* Acceleration of Catalytic Activity of Silica Gels of Different Porosity. (In Russian.) L. Kh. Freidlin, I. E. Nemiark, G. A. Fridman, and R. Yu. Sheinfain. Izvestiya Akademii Nauk SSSR (Bulletin of the Academy of Sciences of the USSR), Section of Chemical Sciences, Jan.-Feb. 1951, p. 80-84.**

Presents results of a comparative investigation of the catalytic properties of activated and non-activated test specimens of different porosity in the hydrolysis of chlorobenzene. Influence of different factors, such as type of activator, degree of porosity, etc., on activity of silica gel catalyst was studied. Emphasizes the influence of the copper activator and mechanism of such activation. Data are comprehensively tabulated and charted.

*Inst. Org. Chem., AS USSR*

AS - S.S.A. METALLURGICAL LITERATURE CLASSIFICATION

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CA

The active structure of the nickel-hydrogen catalyst.  
L. Kh. Fridlin and N. I. Ziminova (Acad. Sci. U.S.S.R., Moscow). *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1961, 145-0. — In a skeleton Ni catalyst, prep. by leaching a 50% Ni-Al alloy at 105°, the atom ratio  $H_{ads}:H_{des}:Ni$  was found = 1:3.6:9 (subscripts ads and des referring to adsorbed and dissolved H, resp., detd. by the previously (C.A. 45, 1830A) described method of selective hydrogenation of org. compds.).  $H_{ads}$  gives the measure of the active centers present at the surface. That this is directly related to the amt. of the structural  $H_{des}$  is shown experimentally by progressive removal of  $H_{des}$  with the aid of increasing amts. of 1-methyl-1-cyclopentene (I), in the absence of free  $H_2$ . For complete removal of the  $H_{des}$  corresponding to the given amt. of I, 90 min. is enough. The amt. of I, adsorbed by a given sample of the Ni catalyst (2.33 g., contg. 47.4 ml.  $H_{ads}$  and 177 ml.  $H_{des}$ ) proves to be a linear function of the remaining  $H_{des}$ . Likewise, the catalytic activity in hydrogenation of allyl alc. is a linear function of  $H_{des}$ , and both adsorption of I, and catalytic activity fall to zero when all the  $H_{des}$  is removed by a sufficient amt. of I. The same behavior was observed with the use of  $CH_2=CHOBu$  (II) as H-remover; allyl alc. had been previously shown to remove only  $H_{ads}$ , but not  $H_{des}$ . The straight lines representing the change of adsorption and of catalytic activity, as a function of the remaining  $H_{des}$ , have the same slope; in other words, the ratio  $H_{ads}/H_{des}$  remains const., and, in the given instance, is = 0.27. Both I and II are consumed in equimol. amts., equiv. to the amt. of  $H_{des}$  removed. X-ray diagrams (Fe radiation, 30 kv., 10 mm.) show complete identity of the lattices of active Ni metd. with  $H_{des}$ , and of Ni inactivated by depromotion with II.

- Inst. Org. Chem., AS  
USSR

C. 2  
1481

Poisoning of the silica-gel catalyst by inorganic impurities and by the reactants. I. R. Neimark, L. Kh. Frekhtin, R. Yu. Shostakov, and G. A. Fridman (L. V. Ponomarevskii Inst. Phys. Chem., Acad. Sci. Ukr. S.S.R., Kiev). *Izv. Akad. Nauk S.S.R., Otdel. Khim. Nauk* 1951, 311-16. — Poisoning of a sample of com.  $\text{SiO}_2$  gel with 1%  $\text{HCO}_2\text{Li}$  caused a decrease of the micropore vol. from 0.21 to 0.11 ml./g., and of the sp. surface area from 208 to 161 sq. m./g. In another sample, the same addn. caused a decrease of the total pore vol. from 0.46 to 0.40 ml./g., of the micropore vol. from 0.20 to 0.19 ml./g., and of the sp. surface area from 450 to 309 sq. m./g. In a 3rd sample, the total pore vol. decreased from 0.48 to 0.43, and the micropore vol. from 0.26 to 0.18 ml./g. The vol. of intermediate pore underwent no change. Along with these changes of micropore vol. and sp. surface area, there is also a decrease of the catalytic activity in the gas-phase hydrolysis  $\text{PhCl} + \text{H}_2\text{O} \rightarrow \text{PhOH} + \text{HCl}$ , as illustrated by the following data of yields of  $\text{PhOH}$  and  $\text{HCl}$ , at  $800^\circ$ : unpoisoned  $\text{SiO}_2$  gel (space velocity 388 g.  $\text{PhCl}/\text{l. catalyst/hr.}$ ) 10.7 and 11.2%; poisoned with 1%  $\text{HCO}_2\text{Li}$  (space velocity 326) 0.2 and 0.8; poisoned with 1%  $(\text{AcO})_2\text{Pb}$  (space velocity 572) 0.5 and 0.7. The poisoning is reversible; with an imported (German)  $\text{SiO}_2$  gel, impregnated with  $\text{CoCl}_2$ , the sp. surface and the catalytic activity were increased upon elution of the  $\text{CoCl}_2$ . Adsorption of  $\text{H}_2\text{O}$  vapor on the  $\text{SiO}_2$  gels was not detected at either  $300^\circ$  or  $450^\circ$ . At  $480^\circ$ ,  $\text{PhCl}$  was adsorbed without decomp., but  $\text{PhBr}$ , and to an even higher degree,  $\text{PhI}$ , underwent decomp. At  $300^\circ$ , where there was no decomp., adsorption of  $\text{PhBr}$  was 3 times, and that of  $\text{PhI}$  7 times as great as that of  $\text{PhCl}$ . The very much stronger adsorption of  $\text{PhBr}$  and  $\text{PhI}$  as compared with  $\text{PhCl}$  is taken to account for the decrease of the hydrolytic catalytic activity of  $\text{SiO}_2$  gel, unpromoted or promoted with  $\text{CuCl}_2$ , from  $\text{PhCl}$  to  $\text{PhBr}$  and  $\text{PhI}$ , owing to stronger adsorptive poisoning by the latter reactants. N. Thon

FREIDLIN, L. Kh.

Kinetics of dehydration of formic acid on phosphate catalysts and on aluminum oxide. L. Kh. Freidlin and A. M. Levit (Inst. Org. Chem., Acad. Sci. S.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1951, 625-30; cf. *Zhur. Obshchei Khim. (J. Gen. Chem.)* 21, 1255 (1951).—Flow expts. were made at a feed rate of 0.16 ml.  $\text{HCO}_2\text{H}$  (82 or 100%)/min., on 20 ml. catalyst (wt. 9-11 g., length of column 6 cm.), with analyses of the gas for CO. The exptl. data (temp., ml. gas evolved per ml.  $\text{HCO}_2\text{H}$ , degree of decompn. in %) are: on  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  with 82%  $\text{HCO}_2\text{H}$ : 167°, 39.2, 8.4; 182°, 82.0, 17.7; 198°, 150.0, 33.7; 201°, 184.0, 40.0; 210°, 242.0, 52.2; 218°, 342.0, 73.8%; on  $\text{Ca}_3(\text{PO}_4)_2$  with 82%  $\text{HCO}_2\text{H}$ : 172°, 20.0, 4.3; 198°, 49.5, 10.7; 200°, 63.7, 13.7; 220°, 121.0, 26.1; 236°, 190.0, 40.0; 248°, 260.1, 50.1; 250°, 303.2, 65.4%; on  $\text{Ca}_3(\text{PO}_4)_2$  with 100%  $\text{HCO}_2\text{H}$ : 172°, 39.4, 0.6; 270°, 591.0, 100.0%. The gas evolved, in all cases, is 100% CO. The activation energies  $E$  (kcal./mole) and preexponential factors  $k_1$  are (with 82%  $\text{HCO}_2\text{H}$ ), on  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , 17.6 and  $4.8 \times 10^4$ , and on  $\text{Ca}_3(\text{PO}_4)_2$ , 15.2 and  $5.2 \times 10^4$ . These catalysts are, consequently, highly selective in the sense of dehydration of  $\text{HCO}_2\text{H}$  as against dehydrogenation, and highly active. At a feed rate of 0.22 ml./min., at 270°, 0.91 ml. pure CO were evolved for 1 ml.  $\text{HCO}_2\text{H}$ , as against 93.8% decompn., with only 94.8% CO in the gas, obtained by Graeber and Cryder (*C.A.* 29, 6208) on his best catalyst,  $\text{ThO}_2$  on silica gel at 280°. The phosphates retain undiminished activity after 20 hrs. service. The data for  $\text{Ca}_3(\text{PO}_4)_2$  fired 6 hrs. at 800° (with 82%  $\text{HCO}_2\text{H}$ ) are: 201°, 31.0, 6.7; 240°, 135.1, 29.1; 254°, 157.0, 33.0; 278°, 293.2, 63.2%; CO content in gas 90.0-90.5%;  $E = 15.2$ ,  $k_1 = 3.5 \times 10^4$ . For  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  heated 1 hr. at 250-300°: 147°, 26.8, 5.0; 157°, 60.0, 10.8; 170°, 104.0, 22.4; 178°, 168.1, 30.3%; CO in gas 100%,  $E = 22.7$ ,  $k_1 = 3.2 \times 10^4$ .

The firing results in a decrease of the rate by one half, with unchanged  $E$ . Preliminary heating to 250-300° increases the rate very considerably, despite some increase of  $E$ . The activity of  $\text{Al}_2\text{O}_3$  is both lower and less selective than that of the Ca phosphates. Exptl. data with  $\text{Al}_2\text{O}_3$  (concn. of  $\text{HCO}_2\text{H}$ , temp., ml. gas evolved/ml.  $\text{HCO}_2\text{H}$ , degree of decompn. of  $\text{HCO}_2\text{H}$  in %, CO content in gas in %) are: 100%: 261°, 112.1, 18.8, 94; 310°, 494.0, 83.2, 83; 72%: 201°, 70.4, 20.2, —; 310°, 362.0, 92.3, —; 52%: 201°, 62.5, 23.0, —; 310°, 280.0, 98.2, —; 39%: 201°, 42.5, 21.2, 83; 310°, 187.6, 94.2, 80. Treatment of  $\text{Al}_2\text{O}_3$  by impregnation with  $\text{K}_2\text{O}$  lowers the selectivity still further, with 7%  $\text{K}_2\text{O}$ , at 203°, the activity was decreased by 30%, and the amt. of CO in the gas from 93 to 73%. Firing of  $\text{Al}_2\text{O}_3$  6 hrs. at 800° lowers its activity by about one half.

N. Thon

PREYDLIN, L. KH.

PA 197T15

USSR/Chemistry - Catalysts

Nov/Dec 51

"Determination of the Relative Adsorption Coefficients of Water and Formic Acid on Silica Gel,"  
L. Kh. Preydlin, A. M. Levit, Inst Org Chem, Acad  
Sci USSR

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 6, pp 799-805

In view of the fact that dehydrated  $\text{SiO}_2$  gel exhibits sharply lowered catalytic activity in dehydration of  $\text{HCOOH}$ , vapor phase hydrolysis of aromatic Hal deriva, etc, a study of relative adsorption of water and  $\text{HCOOH}$  seemed advisable.

197T15

USSR/Chemistry - Catalysts (Contd)

Nov/Dec 51

This study was carried out on untreated (I), calcined (II), and promoted (III)  $\text{SiO}_2$  catalyst from the Voskresensk Chem Combine. Below 3000,  $\text{HCOOH}$  on I is adsorbed less strongly than water. With II, the relative adsorbability of  $\text{HCOOH}$  drops still lower. It rises sharply on silica gel promoted with  $\text{K}_2\text{CO}_3$ . The coeff of relative adsorption varies with temp. At low temps, the relative adsorbability of water rises.

CA

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Effect of very high pressures on the catalytic properties of aluminum oxide. L. F. Vereshchagin, L. Kh. Frekllig, A. M. Rubinshtein, and I. U. Numanov (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izv. Akad. Nauk S.S.S.R., Khim. Nauk* 1951, 89-18.--- Dehydration runs of EtOH to C<sub>2</sub>H<sub>4</sub> were made in a flow system on 12 ml. of catalyst (tube diam. 15 mm.) in the temp. range 263-320°, at a feed rate of 0.16 ml./min. (space velocity 0.96 l./l. catalyst). The C<sub>2</sub>H<sub>4</sub> content in the gas was at least 97% throughout. Stability of the catalysts was tested by the constancy of the rate of the gas evolution, v (ml. STP/ml. EtOH); the necessary regeneration was done with air, 2 hrs. at 525°. Fresh Al<sub>2</sub>O<sub>3</sub> pptd. from Al(NO<sub>3</sub>)<sub>3</sub> with NH<sub>4</sub>OH, washed, and dried at 110° (catalyst I) showed a low initial activity, activation energy  $E = 82.5$  kcal./mole; after 2 hrs. activation with air, 2 hrs. at 525°, the activity rose,  $E$  falling to 16.0. After runs, without regeneration,  $E$  rose to 19.2, and, after 5 days stay with the reaction products,

over →



to 43.4. Regeneration restored the activity almost completely, and  $E$  to 18.0. Renewed 2-day contact with the reaction products again increased  $E$  to 32.0. That this deactivation of the catalyst is due to slow polymerization of the  $C_6H_6$  to a film on the surface, and depends on the length of the contact between the catalyst and the products, was demonstrated directly: there is no deactivation if the products are removed quickly, e.g., by passing  $N_2$  for 10 min. at  $300^\circ$ ; after 48-hr. stay under  $N_2$ , the catalyst showed almost the original activity, with  $E = 17.5$ . If  $N_2$  is passed at a somewhat lower temp.,  $200-250^\circ$ , and the catalyst left overnight under  $N_2$ , it has  $E = 23.6$ . Passing of  $N_2$  at a still lower temp. is not sufficient to prevent polymerization, and then subsequent treatment with  $N_2$  at  $400^\circ$  lowers  $E$  only to 21.6 kcal./mole.  $\gamma\text{-Al}_2\text{O}_3$  not specially dehydrated, and compressed under 2.5 atm. (catalyst II),  $E$  was initially 22.4, and after activation at  $505^\circ$ ,  $E$  was 17.4. Repeated activation produced no further change of the activity. With  $\text{Al}_2\text{O}_3$  dehydrated 1-11 hrs. at  $505^\circ$  and then compressed under 20 atm., activation at  $505^\circ$  doubled the activity. Further regeneration produced no further change. On standing overnight in contact with the reaction products,  $E$  increased to 26.5 in prolonged expts. at  $280^\circ$ , with a total of 2.9 ml.  $\text{C}_6\text{H}_6$  passed; the compressed catalyst proved to maintain a stable activity for 23-24 hrs. (both before and after regeneration) against 13-13 hrs. with the uncompressed specimen. In a tray expt., compression under 20 atm. produces no phase changes; all specimens showed the same pattern of face-centered cubic  $\gamma\text{-Al}_2\text{O}_3$ . However, compression does produce recrystallization, consisting in an ordering of the atoms and elimination of defects; II and III had the lattice constant  $a = 3.907 \text{ \AA}$ . (the tabular value), as against  $a = 3.761 \text{ \AA}$  with I. The dimension of the elementary crystallites, 32.3  $\text{\AA}$ . in I, falls to 30.8 in II and III. The observed vol. contraction by a factor of 2 is consequently not a result of a change of structure of the primary crystallites, but of secondary formations. These changes affect primarily macroporosity and have no bearing on the microporosity which is significant for the catalytic activity. The initial activities of the fresh catalysts increase in the order I, II, III; after regeneration, the order of increasing activities is II, I, III, with approx. equal  $E$  in all 3 catalysts. The relatively low activity of catalyst II is presumably due to the difficult dehydration of an already compressed specimen. After prolonged regenerating treatment, the activity of II rises above that of I. The greater stability of the compressed II and III shows that their surface is less active in catalyzing polymerization.

191T23

USSR/Chemistry - Catalysts

Jul 51

"Investigation of the Kinetics of Dehydration of Formic Acid on Silica Gel," L. Kh. Freydlin, A. M. Levit

"Zhur Obshch Khim" Vol XXI, No 7, pp 1255-1264

Investigated kinetics of dehydration of HCOOH at 200-300° C on differently treated silica gel specimens, whose apparent activation energies were in the order: thermally deactivated > active > promoted with inorg admixts. Gas product was 98-99% CO. Reached conclusions as to uniformity, location of active centers,

191T23

USSR/Chemistry - Catalysts (Contd)

Jul 51

effectiveness of different inorg admixts. Calcd number of active centers per 1 g silica-gel, found it to be 10 times as great for 1 mol HCOOH as for 1 mol EtOH.

FREYDLIN, L. Kh.

191T23

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**Poisoning of hydrogenation-dehydrogenation catalysts in the light of the theory of their active structure.** L. Kh. Freidlin and N. I. Ziminova (Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 70, 661-4 (1961).—Reasons are enumerated why poisoning of a great variety of hydrogenation-dehydrogenation catalysts (Pd, Pt, Ni, Co) with a great variety of catalyst "poisons" (O, S, Se, Te, P, As, Sb, Bi, Cl, Br, I, and their compds.) does not, as is commonly and generally assumed, consist in absorptive "blocking" of active centers, but is due to removal of dissolved H that is an essential promoter of the catalysts. The poisons listed are all highly reactive towards H. The poisoning effect of this great variety of poisons cannot be due to a reaction with the metal, especially as I, which does not react with Pt-group metals at all, is a catalyst poison even at room temp. That, in all these instances, the "poisoning" consists simply in "depromotion" through removal of H, is further corroborated by the irreversible nature of that poisoning, and the necessity of renewed hydrogenation to restore the catalytic activity. Further proof is provided by the stoichiometric proportion between the consumption of the poison and the amt. of dissolved H, and the simple relation between the amt. of poison intro-

duced and the lowering of the activity. The very strong poisoning effect of H<sub>2</sub>S can be explained by a chain reaction of the type  $\text{H}_2\text{S} + \text{H} \rightarrow \text{H}_2 + \text{HS}$ ;  $2\text{HS} \rightarrow \text{H}_2 + 2\text{S}$ ;  $\text{S} + \text{H} \rightarrow \text{HS}$ , etc., owing to which one mol. of H<sub>2</sub>S can bring about the removal of a great no. of H atoms. Regeneration by a stream of H<sub>2</sub> has essentially the effect of satg the catalyst anew with H. The observation of Shulkin, et al. (C.A. 42, 4437a) that 1-ethyl-1-cyclopentene deactivates the Pt/C catalyst very rapidly, can be readily explained by a consumption of the dissolved H, in agreement with the easy zero-order hydrogenation of cyclopentene at room temp under ordinary pressure; this hydrogenation takes place even in the absence of H<sub>2</sub>, solely at the expense of the dissolved H, and results in complete poisoning of the catalyst. In the hydrogenation of 10 ml. of an 8.18% soln. of 1-methyl-1-cyclopentene (I) in C<sub>6</sub>H<sub>6</sub>, on 2.33 g. Ni, the initial rate of absorption of H<sub>2</sub> was 2 ml./min.; after 90 min., that rate fell to 0.8 ml./min., and, after another 90 min., to 0.2 ml./min. The I content of the soln. fell, at these stages, to 5 and to 1.1%, resp. Superficially adsorbed H is only loosely bound and, being consumed first, protects active centers against depromotion, as long as H<sub>2</sub> is supplied from without. Conditions favoring removal of the dissolved H, such as high temp., vacuum, or a stream of extraneous gas, depromote the catalyst. By practical experience in dehydrogenation and hydrogenation reactions, the strength of the bond between the dissolved-H promoter and the catalyst decreases in the order Pt > Ni > Pd. Acceptors of dissolved H have a depromoting action. The practice of carrying out dehydrogenation in a stream of H<sub>2</sub> is dictd by the advisability of keeping up a const. supply of the promoter.

N. Thom

FREYDLIN, L. KH.

USSR/Chemistry - Catalysts

Nov 51

"Kinetics of Removal of the Promotor from a Skeleton Nickel Catalyst and the Relative Rate of Activation of Hydrogen," L. Kh. Freydlin, K. G. Rudneva, Inst Org Chem, Acad Sci USSR

"Dok Ak Nauk SSSR" Vol LXXXI, No 1, pp 59, 62

In expts on the hydrogenation of benzoinone, established that hydrogen is present on the catalyst in 2 forms, dissolved hydrogen (I) and adsorbed hydrogen (II). It acts as catalyst promoter: When due to rapid rate of supplying benzoinone, slow rate of supplying H<sub>2</sub>, or

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insufficient quantity of catalyst, I is used up, the catalyst is deactivated. The limiting factor is not diffusion of hydrogen, but its activation: The velocity of the reaction of adsorbed hydrogen with benzoinone is much greater than the rate of activation of hydrogen by adsorption. The energy of activation of the reaction seems to be the same with either I or II.

19815

**CIA-RDP86-00513R000413620020-3"**

FREYDLIN, L.Kh.; LEVIT, A.M.

Kinetics of the dehydration of alcohols in the presence of trisubstituted calcium phosphato. Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. '52, 177-84 [Engl. translation].  
(CA 47 no.19:9920 '53)

Promotion of dehydrogenated skeleton nickel. L. Kh. Freidlin and K. G. Rudneva (Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 83, 105-8(1953); cf. C.A. 45, 0029i; 46, 1854g. —The Ni catalyst, prepel. by 2 hrs. leaching of a 60-65% Ni-Al alloy at 100°, was dehydrogenated by 1-hr. treatment with a 3% soln. of benzoquinone at 60° under Ni, and then again satd. with H<sub>2</sub>. At 60°, the dehydrogenated catalyst was able to take up an amt. of H<sub>2</sub> up to about 45% of the amt. present in the original catalyst prior to its dehydrogenation. At a still higher temp., 90°, the amt. of H<sub>2</sub> taken up remained about the same, only the time necessary for it was

shorter. The rehydrogenated catalyst reduces benzoquinone; consequently, the H<sub>2</sub> taken up is active. The activity of the reactivated catalysts was tested in hydrogenation at 20°, of vinyl phenyl ether (in alc. soln.), eugenol (in alc. soln.), and camphorquinone (in CCl<sub>4</sub> soln.). With the latter, a distinct lowering of the activity is observed after one half of the equiv. amt. of H<sub>2</sub> (relative to the amt. of the quinone) has been spent; this, evidently, corresponds to the beginning of hydrogenation of the 2nd CO group. The 1st stage of the reaction follows a 2nd-order law. In all cases, the activity of the catalyst regenerated at 60° is lower than that of the original, nondehydrogenated catalyst. In some expts., with vinyl phenyl ether, the activity of the regenerated catalyst remains fairly const. over the course of the hydrogenation, and draws close to that of the original catalyst. This shows that, although the catalyst becomes deactivated in the course of the reaction, it is also reactivated. The hydrogen in the reacting mixt. is not merely a reactant, but it also plays the role of promoter which regenerates the catalyst in the very course of the reaction. N. Thon

USSR/Chemistry - Hydrocarbons

Jan/Feb 52

"The Kinetics of the Dehydration of Alcohols in the Presence of Three-Substituted Calcium Phosphate,"  
L. Kh. Freydlin, A. M. Levit, Inst of Org Chem,  
Acad Sci USSR

"Iz Ak Nauk, Otdel Khim Nauk" No 1, pp 163-171

Dehydration of alcs in presence of 3-substituted calcium phosphate proceeds highly selectively, with the gas contg 98-99% unsatd compds. Secondary alcs are most easily dehydrated by this method, iso-alcs less easily, and normal alcs least. The rate of

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dehydration of normal alcs decreases with increasing mol wt. Calcination of the phosphate catalyst decreases its activity. On substitution of the hydrogen at the  $\alpha$  and  $\beta$  carbon atoms of ethanol, the activation energy is reduced, as was found also with the use of other catalysts.  $K_2CO_3$ , which acts as promoter for phosphate catalyst in dehydration of  $HC(OH)$ , poisons this catalyst in the dehydration of alcs.

208714

FREYDLIN, L. KH.



FREYDLIN, L. Kh.

U S S R .

/ Effect of pressing on the character of porosity, catalytic properties, and chromatographic activity of silica gel. L. Kh. Freydlin, L. E. Vereshchagin, I. E. Nelmark, I. U. Numangy, and R. Yu. Sheinfaiz. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1953, 841-6 (Engl. translation).—See C.A. 48, 4929f. H. L. H.

U S S R .

✓ Stability of skeletal nickel catalyst at elevated temperature. L. Kh. Freidlin and K. G. Rudneva. Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1953, 987-88 (Engl. translation).—See C.A. 48, 6217d. H. L. H.

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Stability of skeletal nickel catalyst at elevated temperature. L. Kh. Freidlin and K. G. Rudneva (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 1111-15; *J. C.S. 46*, 1854g. Thermal deactivation of skeletal (Raney) Ni in N atm. and in *vacuo* was examd. In N atm. in absence of org. matter the catalyst has high stability, and its activity is not lowered by 2 hrs. at 300°, only at 400° or higher does its activity decline. Heated in *vacuo* the catalyst loses its activity more rapidly than it does in N atm. Thus the main reason for decline of Ni activity under usual hydrogenation conditions is apparently not recrystn. but destruction of the active surface owing to chem. dehydrogenation and blocking.

G. M. Kosolapoff

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Reaction of acid anhydrides with formates. I. Decomposition of formates by acetic anhydride. L. Kh. Fridlin, A. A. Balashin, and N. A. Lokhanova. *Izv. Akad. Sci. U.S.S.R. Chem. Ser.* 1953, 1, 341-2 (1953). Salts of  $\text{HCO}_2\text{H}$  react with 1 mole  $\text{Ac}_2\text{O}$  yielding  $\text{AcOH}$ ,  $\text{CO}$  and the corresponding metal acetates. The cation of the salt affects the decomn. The reaction proceeds in the cold; with the  $\text{Ti}$  salt, it is complete at  $00^\circ$ , with the  $\text{Na}$  salt at  $80^\circ$ , and with the  $\text{Li}$  or  $\text{Mn}$  salts at  $110^\circ$ . Other formates are incompletely decompt. ( $\text{Zn}$  salt) or do not react at all ( $\text{Ca}$  salt). The reaction is accelerated by org. bases with a tertiary N atom, as well as by acids like  $\text{AcOH}$ . Strychnine is a more effective catalyst than  $\text{AcOH}$ . Addn. of such catalysts not only accelerates the reaction but may affect the position of the reactivity of the salt in the above list; particularly susceptible in this respect is the  $\text{Li}$  salt. The kinetic curves of the reaction show max., which are characteristic of autocatalytic reactions. It is suggested that the reaction proceeds through an initial noncatalytic stage, after which the  $\text{AcOH}$  formed catalyzes the process. Cf. Whitford, *C.A.* 20, 363. II. Effect of the nature of the anhydride. *Ibid.* 360-4. The reaction of  $\text{Ti}$  and  $\text{Na}$  formates described in preceding abstr. is general for all aliphatic anhydrides. The  $\text{Ti}$  salt reacts even at room temp. and this reaction may be employed for qual. detection of the anhydrides. Anhydrides of dibasic acids require elevated temp. for reaction, while anhydrides of unsatd. dibasic acids do not react, nor do coumarin, phthalimide, or lactide. It was shown that, under the conditions described by Tsakalotos (*C.A.* 4, 2304), it is impossible to isolate the product of addn. of  $\text{HCO}_2\text{Na}$  and  $\text{Ac}_2\text{O}$ ; the cryst. product is apparently  $\text{AcONa} \cdot \text{AcOH}$ , and is completely free of formate.

G. M. Kosolapoff

FREYDLIN, L. Kh., A. A. Balandin and E. A. Lekhanova

Interaction of Acid Anhydrides with Formates. II. Effect of the Nature of the Anhydride, page 350

Sbornik statey po obshchey khimii (Collection of Papers on General Chemistry), Vol I, Moscow-Leningrad 1953, pages 762-'766

Inst of Organic Chemistry, Acad, Sci USSR

FREYDLIN, L. KH.

USSR/Chemistry - Catalysts

Card 1/1 : Pub. 40 - 21/22

Authors : Freydlin, L. Kh.; Vereshchagin, L. F.; Neymark, I. E.; Numanov, I. U.;  
and ~~Sneyfnayn~~, R. Yu.

Title : Effect of compression on the porosity, catalytic properties and chromatographic activity of silica gel

Periodical : Izv. AN SSSR. Otd. khim. nauk 5, 945-950, Sep-Oct 1953

Abstract : The effect of 20,000 atm pressures on the change in porosity, adsorbability and catalytic properties of silica gel was investigated. The chromatographic activity of silica gel compressed at 20,000 atm was found to be about 25% lower than the activity of non-compressed s. g. The greatest reduction (almost 50%) in specific sorption volume of pores (total volume of micro- and transient pores) of large porous silica gel was observed at 5000 atm. but its specific surface area remained unchanged. Maximum reduction in specific sorption volume of pores of micro-porous silica gel was established during compression of latter at 10,000 atm. Five USSR references (1949-1952). Tables, graphs.

Institution : ...

Submitted : December 13, 1952

FREYDLIN, L. Kh.

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The influence of compression on the properties of solid catalysts. L. Kh. Freydlin, L. P. Verezhchagin, and I. U. Nuzhakov. *Dokl. Akad. Nauk SSSR*, Moscow, 1968, Vol. 188, No. 10, 1819-1821. (Chem. Abstr. 68:10111b)

of chlorobenzene (III) at 450-600°. Activity of the same wt. of catalyst changed 1.09, 1.27, 0.51, 0.50, 0.27, 1.00, and 0.65-fold, resp. Compression of the catalysts did not change the activation energy of the above reactions. De-

which was compressed in ampur made from pure. The app. was described previously (cf. Ref. 40, 41, 42). Compression to 30,000 atm. decreased the vol. of Ag<sub>2</sub>O catalyst 1.4, PbO<sub>2</sub> 1.5, TiO<sub>2</sub> 2.0, ZnO 3.3, CdO 1.2, and macroporous (I) or microporous (II) silica gel 2.0 and 1.5, resp. The catalysts in the state of compression were used for the catalytic reactions of chlorobenzene with hydrogen and for the reaction of chlorobenzene with hydrogen.

after compression. Such a low surface area, which is characteristic of pores, hence their sp. activity did not change. The results of the experiments show that compression changes the lattice structure of the catalysts. The catalysts of Ag<sub>2</sub>O and PbO<sub>2</sub> decreased with compression from 1.09 to 0.51 and 0.50, respectively, which is due to the decrease in the surface area of the catalysts.

compression did not change the activation energy of the reactions.

FREYDLIN, L. K.

USSR.

The metal-hydrogen nature of certain hydrogenation catalysts. L. Kh. Freidlin and K. G. Rudneva (Inst. Org. Chem., Acad. Sci. U.S.S.R.). *Doklady Akad. Nauk S.S.R.* 91, 569-72 (1953); cf. C.A. 48, 14042i, 14043e. J. Rovtati Leach

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FREYDLIN, L.Kh.

U.S.S.R.

The nature of the activity of an iron skeleton catalyst.  
 I. Kh. Freydlin and K. G. Rudneva. *Doklady Akad. Nauk S.S.S.R.* 91, 1171-4(1953); cf. *C.A.* 45, 8031a.—By the method described earlier (cf. *C.A.* 46, 1854g) the relation between the activity of a skeletal Fe catalyst and its H content was detd. The catalyst was prepd. by leaching Fe-Al alloys with NaOH. A catalyst prepd. from an alloy contg. 50% Al is not very active for hydrogenation (it contains 20 ml. H per g. of catalyst). That prepd. from a 60% alloy is 10 times as reactive (20 ml. H per g. of catalyst) and from a 68% alloy — 20 times as reactive (73 ml. H per g. of catalyst). If the catalyst is treated with benzoquinone, it becomes completely inactive and does not adsorb H. This verifies conclusions reached earlier on the metal-H nature of the catalyst. It was also established that the metal-H bond is more stable in the Ni catalyst than in the Fe catalyst.  
 J. Roytar Leach

FREYDLIN, L. K. H.

62 ✓ Reduction of the metal-hydrogen component of the active surface of a nickel catalyst. L. Kh. Freidlin and K. G. Rudnaya. *Doklady Akad. Nauk S.S.S.R.* 91, 1349-52 (1953); cf. *C.A.* 48, 14042i; 49, 9839f.—The effect of reducing a deactivated skeleton Ni catalyst with H at increased temp. was studied. Expts. in which the catalyst was treated with H for 2 hrs. were carried out at 200, 250, 300, 400, and 600°. The catalyst reduced at 300° had an activity equal to that of the freshly prepd. active catalyst. If the time of reduction was decreased, the catalytic activity was negligible. The catalytic activity of the sample was not a function of the H content but of the stability of the metal-H bond. J. Rovtar Leach

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Influence of compression on the properties of dehydrogenation and dehydration catalysts. I. V. Vereshchagin, I. Kh. Freidlin, I. V. Nuzinov, and S. G. Kulikov (*Izvestia Akad. Nauk SSSR*, 1981, 154-161). --The influence of pressures up to 20,000 atm on the properties of  $ZnO$ ,  $TiO_2$ ,  $ThO_2$ , and  $Ca_3(PO_4)_2$  (catalysts in dehydrogenation and dehydration reactions) is studied. The bulk volume of the powders compressed to 20,000 atm decreases by factors 3-3, 2-4, 1-5, and 2-2 for  $ZnO$ ,  $TiO_2$ ,  $ThO_2$ , and  $Ca_3(PO_4)_2$ , respectively. Compression does not alter the selectivity of  $ZnO$  in dehydrogenation of  $HuOH$  and  $Ca_3(PO_4)_2$  in dehydration of formic acid and does not change the ratio of dehydrogenation and dehydration reaction rates during decomposition of  $EtOH$  in the presence of  $ThO_2$ . However, in the presence of compressed  $TiO_2$  catalyst this ratio is smaller than for uncompressed  $TiO_2$ . This change is caused by the decrease of porosity of  $TiO_2$ , which renders the desorption of the dehydrogenation product more difficult. The energy of activation is not affected by the compression of catalysts but their activity per unit wt. decreases with exception of  $ThO_2$ . The activity per unit of vol. increases for all catalysts with the exception of  $Ca_3(PO_4)_2$  for which it decreases by a factor of 2. Cryst. structure of the compressed catalysts, as determined by X-ray photography, is not affected by pressure. S. K. LACHOWICZ

FREYDLIN, L. N.

USSR

The metal-hydrogen nature of the skeletal nickel catalyst  
L. N. Freydlin and K. G. Rudnaya, *Bull. Acad. Sci.*  
U.S.S.R., Div. Chem. Sci. 1954, 417-21 (Engl. translation).  
—See C.A. 48, 14042i. H. J. H.

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